VOL. XII. 1907

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TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

VOLUME XII.

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TWELFTH GENERAL MEETING

NEW YORK CITY, OCTOBER 17, 18, 19, 1907.

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VOLUME XII. 1907

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

PROCEEDINGS

CONDENSED MINUTES OF THE TWELFTH GENERAL MEETING OF THE SOCIETY, HELD IN NEW YORK CITY, OCTOBER 17, 18, 19, 1907.

(Number of members registered, 153; guests, 195; total, 348.)

SESSION OF OCTOBER 17th

The meeting of the Society opened in the lecture hall of the Chemists' Club, 108 West Fifty-fifth Street, New York City, at 8 P. M., at which hour the President and other officers of the Society held a reception for members, guests and friends of the Society.

At 8.40 P. M., Vice-President Doremus in the chair, Dr. Geo. F. Kunz, of New York City, gave an illustrated lecture on "Diamond and Moissanite—Natural, Artificial and Meteoric," which is printed in these Transactions.

At 9.30 P. M., Mr. E. G. Acheson delivered a lecture on "Deflocculated Graphite," with demonstrations and experiments, which is printed in these Transactions.

During the evening there was on exhibition in the hall a number of novelties in the chemical, metallurgical and instrumental line, shown by several progressive firms in these lines of business.

SESSION OF OCTOBER 18th

The meeting was called to order at 9 A. M. in the lecture hall of the Chemists' Club, President C. F. Burgess in the Chair.

Papers by Albert E. Greene and F. S. MacGregor (read by Mr. MacGregor), Jos. W. Richards, H. N. Potter, A. B. Albro, O. P. Watts (read by Jos. W. Richards), Gustave Gin (read by E. F. Roeber), Gustave Gin (read by Jos. W. Richards), C. E. Baker, F. A. J. FitzGerald, S. A. Tucker, A. Doty and R. W. Cauchois (read by S. A. Tucker), and W. R. Mott (read by Jos. W. Richards)—were communicated, as published in full in the Transactions.

After lunch, about 200 participated in a visit to East Orange, N. J., where Mr. T. A. Edison received the visitors and conducted them through his laboratories.

In the evening, 120 attended a banquet in the Liederkranz Hall. A flash-light photograph taken there, reproduced in half-tone and printed with Dr. Potter's "Monox" ink, is inserted as a frontispiece to this volume.

SESSION OF OCTOBER 19th

The meeting was called to order at 9 A. M. in the lecture room of Earl Hall, Columbia University, President C. F. Burgess in the Chair.

Papers by J. W. Turrentine (read by S. A. Tucker), H. Schlundt, H. W. Gillett (read by S. A. Tucker), E. E. Free, H. E. Patten, G. H. Hulett and L. H. Duschak (read by L. H. Duschak), H. N. Potter, H. S. Carhart and F. J. Mellencamp (read by C. F. Burgess), O. W. Brown and R. R. Sayers, and A. S. Cushman—were communicated, as published in full in the Transactions.

At the close of the business session, Prof. Jos. W. Richards (seconded by Carl Hering) moved the hearty thanks of the Society be tendered to Mr. Thos. A. Edison, the United States Metals Refining Co., the Electrical Testing Laboratories, the officers of the Pennsylvania Railroad power plant, the officers of Columbia University, the Chemists' Club, the Liederkranz Society, and to the Local Committee of the Society, for their courtesies and efforts in making and adding to the success of this meeting. The motion was carried unanimously.

After luncheon, excursions were taken by some to the Elec-

trical Testing Laboratories, by others to the new Pennsylvania Railroad power plant, Long Island City, and by nearly 150 others to the works of the U. S. Metals Refining Co., at Chrome, N. J., where copper matte smelting, converting, electrolytic refining, and the electrolytic refining of silver bullion, were seen.

In the evening, the Chemists' Club tendered a "smoker" to the Society, which was largely attended, to the pleasure and profit of the guests.

Members Elected and Qualified.
JULY-DECEMBER, 1907.

July 31, 1907: Franz Roessler, Perth Amboy, N. J.; Eugene Haanel, Ph.D., Ottawa, Canada; L. D. Vorce, Detroit, Mich.; Herschel C. Parker, Brooklyn, N. Y.; John W. Brown, Ph.D., Cleveland, Ohio; John G. Kremers, Milwaukee, Wis.

August 31, 1907: Remo Catani, Portoferraio, Elba, Italy; Wm. Acheson Smith, Niagara Falls, N. Y.; Albert E. Greene, Heroult-on-the-Pit, Baird, Shasta County, Cal.; Hy. L. Kohler, St. Louis, Mo.; Horace M. Engle, Roanoke, Va.; Dr. Louis Liebmann, Frankford a. Main, Germany; Francis C. Frary, Minneapolis, Minn.

September 28, 1907: Walter G. Clark, New York City; George F. Kunz, Ph.D., New York City.; Harvey E. Walters, Altoona, Pa.; Frank S. MacGregor, Hyde Park, Mass.

October 17, 1907: Delos C. Giles, Elmira, N. Y.; Louis I. Waldman, Albany, N. Y.; Louis V. Emanuel, Maurer, N. J.; Noel Statham, Mechanicsville, N. Y.; Frederico Giolitti, Ph.D., Rome, Italy; Edwin F. Northrup, Philadelphia, Pa.

November 26, 1907: William H. Bassett, Torrington, Conn.; H. Clyde Snook, A.M., Philadelphia, Pa.; John Clement Bradley, Torrington, Conn.; William C. Geer, Akron, Ohio; Dr. Georg Langbein, Leipzig, Germany; Axel O. Appelberg, Ph.D., Schenectady, N. Y.; Colin G. Fink, Ph.D., Schenectady, N. Y.; Amos G. Reeve, Niagara Falls, N. Y.; Jasper Whiting, Rumford Falls, Me.; William D. Crumbie, New York City; Edward J. Lavino, Philadelphia, Pa.; A. M. Williamson, Niagara Falls, N. Y.; A. Bernhard Draeger, Draeger Werke, Lubeck, Germany; Clayton H. Sharp, New York City; Jacob Hasslacher, New York

City; Robert Deissler, Berlin, Germany; Frank Hemingway, New York City; Arthur J. Hudson, Cleveland, Ohio; George Morey, Jr., Minneapolis, Minn.; Roland Calberla, New York City; Prof. Alexander Krakau, St. Petersburg, Russia.

December 27, 1907: John L. Polk, Troy, N. Y.; Robt. H. Hartley, Pittsburgh, Pa.; Hugo J. Wichmann, St. Paul, Minn.; Herbert A. Baker, Paulsboro, N. J.; Meyer Schamberg, Philadelphia, Pa.; Wilbur F. Hurlburt, New York City; Fredrik V. L. Hiorth, Christiania, Norway; Lewis E. Saunders, Niagara Falls, N. Y.; James M. Neil, Toronto, Canada; Franz H. Hirschland, New York City; Arthur B. Lamb, New York City.

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A lecture delivered at the Twelfth General Meeting of the American Electrochemical Society, in New York City, October 17, 1907. President C. F. Burgess in the chair.

DEFLOCCULATED GRAPHITE.

By Edward Goodrich Acheson.

In the year 1901 I was engaged in a series of experiments having as their object the production of crucibles from artificial graphite. In this work I was led into a study of clays. What I learned may be briefly stated as follows:

First. The American manufacturers of graphite crucibles imported from Germany the clay used by them as a binder of the graphite entering into the crucibles.

Second. The German clays are much more plastic and have a greater tensile strength than American clays of very similar chemical composition.

Third. Residual clays—those found at or near the point at which the parent feldspathic rock was decomposed—are not, in any sense, as plastic or strong as the same clays are when found as sedimentary clays at a distance from their place of origin.

Fourth. Chemical analysis failed to account for those decided differences.

I reasoned that the greater plasticity and tensile strength were developed during the period of transportation from the place of their formation to their final bed, and I thought it might be due to the presence of extracts from vegetation, the washings from the forests being in the waters which carried them.

I made several experiments on clay with extracts of plants, tannin being one of them, and I found a moderately plastic, weak clay when treated with a dilute solution of gallo-tannic acid, or extract of straw; was increased in plasticity, made stronger—in some cases as much as 300 per cent.; required but 60 per cent. as much water to produce a given degree of fluidity; was caused to remain suspended in water, and was made so fine that it would pass through a filter paper. Being acquainted with the record of how the Egyptians had the "Children of Israel" use straw in

the making of bricks, and how they substituted stubble for straw, and believing it was not used for any benefits derivable from the fibers but for the vegetable extract, I called clay so treated "Egyptianized clay."

Having, in 1906, discovered a process of producing a fine, pure, unctuous graphite, I undertook to work out the details of its application as a lubricant. In the dry form, or mixed with grease, it was easy to handle, but I wished it to enter the entire field of lubrication as occupied by oil. In my first efforts to suspend it in oil I met the same troubles encountered by my predecessors in this line of work—it would quickly settle out of the oil. It obeyed the same laws governing the natural product.

So things stood until the latter part of 1906, when the thought occurred to me that tannin might have the same effect on graphite that it did on clay. I tried it with satisfactory results, the effect being obtainable with the natural graphites as found in the Ticonderoga and Ceylon varieties, and with the artificial product as found in Acheson graphite. It was more easily and cheaply produced when the soft, unctuous variety of my graphite was used, this kind being composed of pseudomorphs of carbide crystals, which had been decomposed in the electric furnace, the resultant graphite being very loose, porous and readily disintegrated and deflocculated. The effect was produced by treating the graphite in the disintegrated form with a water solution of tannin, the amount of tannin being from 3 to 6 per cent., by weight, of the graphite treated. The results are much more pronounced when the mass of graphite, water and tannin has been pugged or masticated for a considerable time, I having carried on this process to advantage continuously, without interruption, for a period of one month. I have also found that while the effect may be produced in a very satisfactory way with distilled water, waters found in rivers, deep wells, etc., are improved by the addition of a trace of ammonia. The presence of carbon dioxide in the water will prevent deflocculation.

The accompanying figures, 1 and 2, show the effect of tannin in suspending graphite. Fig. 1 is that of two test tubes, one containing water, a drop of ammonia and disintegrated Acheson graphite, the other tube containing a similar amount of water, ammonia and graphite, with the addition of a little gallo-tannic

acid. The photograph was taken immediately after the tubes were thoroughly shaken. Fig. 2 shows the same tubes and contents, four minutes having elapsed after being shaken, they not having been disturbed during that interval. These tubes furnish a very clear demonstration of the quick settling of graphite in plain water and the remarkable effect of the presence of tannin.

All of the graphite put into the tube with the tannin did not remain suspended. In fact, in this case, as illustrated, very nearly all of it had settled, only sufficient remaining in the water to give it its blackness. To cause a complete deflocculation and

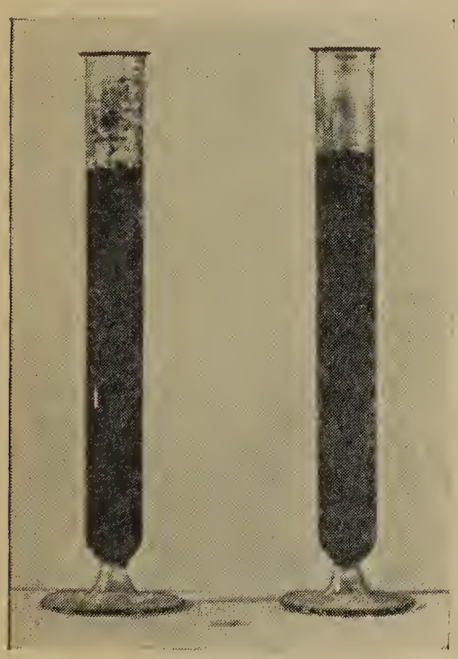


Fig. 1.

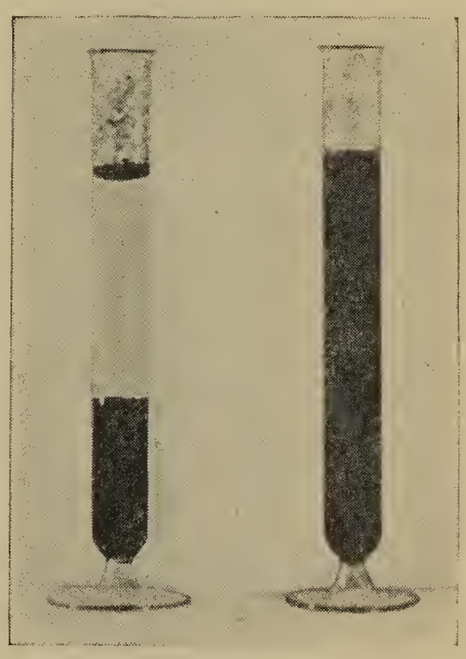


Fig. 2.

suspension of all the graphite necessitates prolonged mastication in the form of a paste, with the water and tannin, and I find that after this mastication has been carried out, the effect is very much improved by diluting the mass with considerable water, and allowing it to remain some weeks with occasional stirring.

After the prolonged masticating, and additional time of exposure of the graphite to the water and tannin, an intensely black liquid is obtained consisting of water, a small amount of tannin and graphite; the latter may be present in varying amounts. In this condition I call the graphite "deflocculated," a state of subdivision much finer than possible of attainment by

mechanical means, one that may perhaps be correctly spoken of as molecular. It is in that condition called "colloidal." This term, however, does not appeal to me, being only the name of a condition or state. The term "deflocculated" is much more readily understood, and, to an extent, it carries with it its own definition. I have found this liquid would pass through the finest of filter papers, and the contained graphite would remain in suspension for weeks and months, apparently for all time. One per cent. of graphite content makes the liquid so thick that

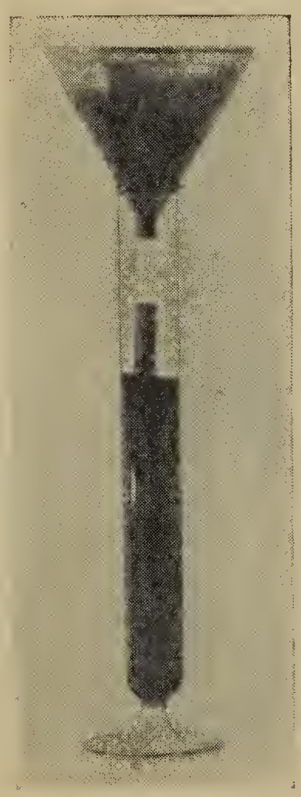


Fig. 3.

Fig. 4.

it runs through the filter paper slowly; reduced to 0.2 per cent., it goes through quickly.

Figs. 3 and 4 illustrate an experiment with water containing 0.2 per cent. graphite. Fig. 3 shows a glass funnel containing a fine filter paper resting in a test tube. In the tube below the funnel is a black liquid, which has passed through the filter paper. This black liquid is water containing 0.2 per cent. deflocculated Acheson graphite. The fact of its having passed through the filter paper leaves no doubt in our minds of the impossibility of separating the water and graphite while in this condition

by ordinary filtration. I have found that the addition of a very minute amount of hydrochloric acid causes the contained graphite to flocculate, *i. e.,* group its particles into masses, so that it will no longer pass through the paper. Fig. 4 shows, as in the former case, the funnel, filter paper and test tube; but now, in the lower part of the tube, below the filter, we find a clear liquid, this being the water in which the deflocculated graphite was formerly suspended, the graphite now being caught entirely in the filter paper above. It will be noticed that the filter paper in Fig. 3 is black on the outside, this having been produced by the deflocculated graphite passing through the paper, whereas the filter paper, as shown in Fig. 4, remains white on the outside, the graphite not having passed through its body.

This effect is obtainable with non-metallic amorphous bodies generally, having been secured with silica, alumina, lamp-black, clay, graphite and siloxicon. An interesting line of thought may be entered into as to the part this effect plays in nature's economy.

This graphite, even after flocculation, is so fine in its particles that when dried *en masse* it forms a hard article. It is self-bonding, like a sun-dried clod of clay.

I have successfully used deflocculated graphite in water, instead of oil, in sight drop-feed oilers and with chain-feed oilers. I have a shaft in my laboratory measuring 2 5/16 inches in diameter, revolving at 3,000 revolutions per minute in a bearing 10 inches long, that had no oil in it for a month, deflocculated graphite and water being the only lubricants used, the feed being by chain, and it ran perfectly. On the same shaft is a similar bearing lubricated with oil, and this ran much the warmer of the two.

A few days after this test was started, a pessimistic friend remarked that just plain, simple water would give the same results, that the presence of graphite was unnecessary. We are influenced by the opinions of others, even when we know or think they are wrong. I emptied the oil out of the second bearing on the shaft, and substituted plain water. The results during the first twelve hours seemed to support the contention of the friend. The next day, after the machine had stood motionless over night, things did not look so well for the water; it was a lame "second," on account of rust, and was hurriedly

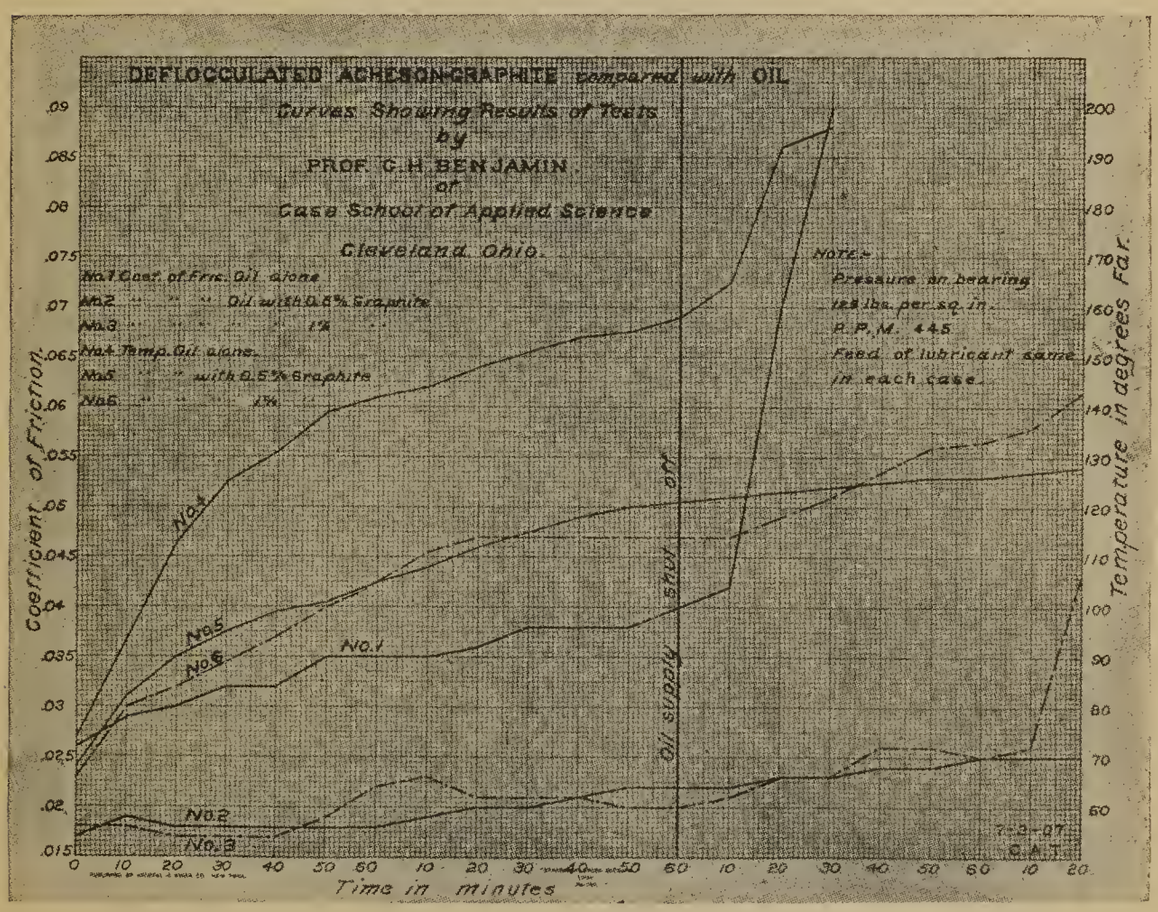
removed. I think I shall not recommend clear water as a permanent lubricant.

Deflocculated graphite in water possesses the remarkable power of preventing rust or corrosion of iron or steel. This characteristic will unquestionably make it of great value for some uses, and while, as yet, little has been done to explore the field, some work has already been accomplished in using it as a cutting compound in screw cutting, and I have been advised, by one large manufacturer, that the results obtained showed it to be equal or superior to lard oil when the water was carrying as little as one-half of 1 per cent. of its weight in graphite. It will readily be understood that while preventing rusting, the high specific heat of the water renders it of great importance, permitting of high speed of the machinery, and, consequently, increased output. Another probable application of deflocculated graphite in water will be as a lubricant for condensing-engine cylinders.

While, as I have stated, deflocculated graphite in water is an excellent lubricant for light work, it has the disadvantage of losing its water by evaporation, and I realized that to utilize the possible advantages of deflocculated graphite, it would be necessary to replace the water with oil; therefore, I set before me the task of accomplishing that result. When it is remembered that a removal of the water by evaporation, previous to its replacement by oil, would cause the contained graphite to assume the condition of a hard, flocculated, self-bonded mass, it will be seen that the problem was not simply one of the evaporation of the water and suspending the resultant dry graphite in oil. A very great deal of difficulty and many discouraging conditions were met with in my attempt to cross this apparently bottomless chasm, and I am pleased to say that I eventually succeeded, and I have been successful in suspending the deflocculated graphite in oil in a dehydrated condition. The graphite will remain suspended in the manner that it formerly did in the water, and we now have in this article a truly new lubricating body.

A new material having been created, as this would evidently seem to be, a new name is necessary, and I have added the initial letters of deflocculated Acheson graphite, d-a-g, to "oil" or "aqua" when the deflocculated graphite is carried in oil or water as the case might be, and have "oildag" and "aquadag" respectively.

Prof. C. H. Benjamin, formerly of the Case School of Applied Science, Cleveland, Ohio, and now dean of the engineering schools of Purdue University, is engaged in making extensive tests to determine the value of deflocculated graphite as a lubricant, and, while these tests are not as yet completed, he has proved that 0.5 per cent., by weight, of this graphite in oil greatly reduces the coefficient of friction and materially extends the life of the oil in which it is suspended as a lubricant. Fig. 5 shows some of the results obtained in his tests with spindle oil,



Initial Friction Oil and 0.5 per cent. Graphite	65 per cent. of oil alone
After 60 m. Friction " " "	55 " "
Friction of Oil increased	54 per cent.
Friction of Oil and Graphite increased	30 "
After lub. was shut off friction of oil increased	125 per cent. in 30 min.
After lub. was shut off friction of oil and graphite increased .	14 " " 80 "

Spindle Oil was used in all tests.

and by a study of them we find that comparing the initial coefficient of friction of plain oil and oil containing one-half of 1 per cent. of graphite, the coefficient of friction of the oil containing the graphite was but 65 per cent. of the plain oil, while after

one hundred and twenty minutes it was but 55 per cent., the friction of the oil having increased 54 per cent., while with the contained graphite it increased but 30 per cent. After shutting off the supply of the lubricant on the bearing, the coefficient of friction of the oil alone increased in thirty minutes 125 per cent., whereas the coefficient of the oil with one-half of 1 per cent. of graphite increased in eighty minutes but 14 per cent. In fact, at the end of the entire run of two hundred minutes, its coefficient of friction was less than the initial friction of the plain oil.

Very extensive and careful tests of "oildag" have also been made at the works of the General Electric Co., Schenectady, N. Y., under the supervision of Mr. W. L. R. Emmett, engineer of the lighting department, and these tests have been corroborative of those made by Prof. Benjamin. They were, however, not made to include measurements of the coefficient of friction, but of the temperature and the surface speed of the shaft in the bearing. The shaft measured 7 inches in diameter, resting in a bearing 21 inches in length, and the test covered both forced lubrication and oil-ring lubrication. Not a great deal of advantage was shown in the case of the forced-feed lubrication, the presence of the graphite holding down the temperature but a very little. In the test on the oil-ring feed, however, very pronounced advantages were shown in favor of the graphite. The graphite content, as used in these tests, was 0.35 per cent. of the weight of the oil, and in the words of the report submitted by Engineer Emmett: "The comparison of oil and oil and graphite with a pressure of 75 to 100 pounds per square inch of projected area of the bearing shows that, with the same pressure and temperature, a shaft can be run from 50 to 100 per cent. faster with the graphite in the oil than with the plain oil." And again: "With the oil-ring bearing, a very large amount can be saved, both in friction and the size of bearing for a given speed and pressure."

I have myself been making tests of the efficiency of my product as a lubricant for automobile gasoline-engine cylinders, with the result that I very materially reduced the consumption of oil. A Packard No. 30 automobile that I am operating ran over 6,000 miles without the necessity of cleaning the spark plugs and, what is still more remarkable, without the necessity of grinding

the valves. It would perhaps be too early to state positively that the use of "oildag" in the gas engine would eliminate the pitting of the valve seats, but the results that I have so far obtained would rather indicate such a possibility. The surfaces produced on the valve seats are remarkable, being much finer than is possible of attainment by any mechanical finishing, the graphite being incorporated in the body of the metal.

DISCUSSION.

Mr. W. Bowman: I would like to ask Mr. Acheson if he has tried the experiment of increasing the density of the water solution; and if so, and if the water solution prevents rusting, what is the advantage of using oil, over water?

Mr. Acheson: I made one brief experiment for the purpose of determining whether or not the presence of deflocculated graphite would increase the density of water, but found a negative result. The presence of the graphite thickens the water, of course, and when in considerable quantity will, as a lubricant, fill up the oil groove usually provided for the distribution of a lubricant in the bearing, and that necessitates using a comparatively small amount with the water, which leaves the water so thin that the film in a bearing will, under heavy pressure, break. In addition to this, there is the fault of rapid evaporation of the water, and for these reasons it seems absolutely necessary that oil be substituted for water.

Dr. H. N. Potter: Mr. Acheson very kindly sent me a sample of "oildag," which I am using mixed with lubricating oil, on my automobile. The mileage per gallon of lubricant is easily twice what it was with the same oil without the addition of "oildag," so I feel that Mr. Acheson has made a great contribution to the art of lubrication. Regarding a molecular subdivision, it seems to me that in such a case, the terms solid, liquid and gas cease to have a sharply defined meaning. Regarding the suggestion of increasing the viscosity of water, it would seem that a suspension of deflocculated graphite in a soap solution might meet the requirements properly, as this would probably have no tendency to rust iron immersed in it.

A lecture delivered at the Twelfth General Meeting of the American Electrochemical Society, in New York City, October 18, 1907; President C. F. Burgess in the chair.

THE DIAMOND AND MOISSANITE—NATURAL, METEORIC AND ARTIFICIAL.

By George F. Kunz, Ph.D.

Introduction.

Within the last fifteen or twenty years there has been developed a remarkable body of researches and discoveries which, although distinct in themselves, are closely related and almost interwoven. These comprise a number of subjects, previously either little understood or entirely unknown, which have now been developed quite extensively; and in the progress of these experiments and discoveries they are found to fit into each other and to lead from one into another in a manner that is curiously interesting. Just as we have explored the ultraviolet invisible spectrum and the infra-red end, so we are now reaching the limits of low temperature and the intense heats of the electric furnace—extremes of heat and cold never encountered in nature. This group of studies includes the great new field of electro-chemistry at enormously high temperatures; of the mutual relations of the different allotropic forms of carbon, and their actual or possible changes from one to another; of the occurrence of carbon in meteorites, and the conditions through which these mysterious bodies have passed before reaching the earth; of the artificial production of diamonds, and the obtaining as an incidental result of experiments toward this object, of new and very hard bodies valuable in the industrial arts.

It has seemed to the writer very desirable to bring together the leading facts of this entire subject, and to describe briefly the principal discoveries in their connection with each other. Of course, in so broad a field, only the points of special interest and importance can be dealt with; the several aspects have been fully presented by others; but the general aspect and the connection of them all has not, perhaps, been set forth before.

In this whole body of recent advances in chemical science, one name stands out above all others—that of the eminent and brilliant French investigator, Prof. Henri Moissan, whose melancholy and untimely death has recently grieved the scientific world and extinguished one of its brightest luminaries. In all these lines of research he has borne a leading part; in many of them he has been the pioneer. He was practically the inventor of the electric furnace, and pursued his experiments with it through many years and in many directions, with results that startled the world. The whole field of the several related branches he also traversed with tireless enthusiasm: the relations of the forms of carbon; their modes of occurrence in nature and their behavior in the laboratory; the structure of meteorites, and their contained minerals, especially carbon; the minerals associated with diamond occurrences on the earth; all these were especially studied by him. His application of these researches and the artificial production of diamond in the electric furnace have immortalized his name; and his numerous and valuable discoveries of new compounds formed at enormous temperatures are no less remarkable. Others, indeed, have had their share in the development of these departments, but he was pre-eminent. Yet he was himself both modest and generous, ready to recognize the work of others, to acknowledge their co-operation, and even to concede priority when there was a fair question—a thing which many are unwilling to do. He loved to follow science for its own sake, not for what it might bring to him; and he placed his results, however commercially valuable, at the disposal of his fellow-men, with no patents or limitations. His was indeed a noble example for others to honor and to imitate.

Carbon Silicide, Meteorites, Diamond, and the Electric Furnace.

It is interesting to note that the great new development of the science of electro-chemistry, with its remarkable results concerning carbon compounds and the diamond, and the study of meteorites in relation to these results, as well as by mineralogists and physicists, should have had their origin and made their great advances together, beginning about 1891. In that year, the late Prof. A. E. Foote described the famous meteorite of

Cañon Diablo, Arizona—if indeed it be a meteorite and not of terrestrial origin, as some have thought—that was found strewn over an area of several miles, in hundreds of pieces, weighing from a fraction of an ounce to a mass of 1,680 pounds.[1] It was in the cutting of a section from one of these masses that certain very hard portions were encountered, which interfered with the saw and even broke it, leaving lines upon the steel itself. These portions proved to be cavities containing extremely hard particles, which, upon examination by Dr. George A. Koenig, of the University of Pennsylvania, were identified as diamond carbon.[2] The presence of carbon in meteoric irons had been already recognized, not in the form of diamond, but as altered to a graphitic or semi-graphitic modification; this was the case with the Cliftonite of Fletcher, from the Youndegin, Australia, meteorite,[3] and in those from Sevier, Cocke County, Tenn., and Arva, Hungary.[4] More recent researches have determined the presence of carbon in several other meteorites, but this was the first recognition of it in the actual form of diamond. The Novy Urej (Siberia) meteorite, of 1886, was largely composed of carbon, with some very hard crystalline particles, but hardly true diamonds.

Dr. Koenig's determination was confirmed shortly afterward by Dr. O. W. Huntington in this country,[5] and by M. C. Friedel in Paris,[6] both of whom submitted the hard, bright particles from the Cañon Diablo iron to exact and thorough tests; and also a little later by Professor Moissan,[7] in a very important article. The crucial test made by the writer and Dr. Huntington together, at the Chicago World's Fair, will be described further on.

At about the same time three independent investigators, E. G. Acheson and A. H. Cowles in this country, and Professor Moissan in France, while studying and developing the electric furnace, produced from it a new compound, which has since

[1] Am. Jour. Sci. (3), **42**, July, 1891, pp. 413-417.
[2] Am. Jour. Sci., l. c.
[3] Miner. Mag., London, **7**, 121 (1887).
[4] Dana, Syst. Min., 1892, 7.
[5] Science, April 8 and July 8, 1892, and Proc. Am. Acad. Arts and Sci., new series, **22**, 252, 253.
[6] Bull. Soc. Fr. de Min., **9**, 258, Dec., 1892.
[7] Comptes Rendus, **116**, 288 (1893).

become widely known and commercially important. This body, which was obtained as a distinct and original discovery in each case, was the compound of silicon and carbon, known both as silicon carbide and carbon silicide, which Acheson introduced into commerce under the name of carborundum.

It is difficult to state just which of the three workers, Cowles, Acheson or Moissan, really first discovered and recognized carbide of silicon, but there is absolutely no question in my mind, or in those of many present, that it was only by the most intense application to study and untiring zeal on the part of Mr. Acheson that the carbide of silicon has been developed from the handful of crystals, which were contained in a small plumber's iron bowl, until he was able to make hundreds of pounds in the most approved electric furnace, and to further grind, prepare and unite this in a hundred ways, until carborundum to-day is one of the most successful abrasives that has ever been recognized, and is not only interesting, but highly lucrative to many.

Mr. Acheson writes to me as follows: "My attention was first drawn to the value of abrasives by a remark made by you (Dr. George F. Kunz) in 1880, when I brought to Mr. Tiffany a product I had made in Menlo Park. In an experiment I made in 1886 I impregnated clay with carbon at a high temperature, and I thought I had increased its hardness. In March, 1891, I undertook to impregnate clay with carbon under the influence of electric heat, for the purpose of forming an abrasive. This experiment was made in an iron bowl, with the result of forming carbide of silicon (carborundum)."

Professor Moissan was a scientist; his main object was to discover, and then leave his work for anyone to develop. He never went further than to establish carborundum, the artificial diamond, and the twenty-eight other carbides with which his name is linked. Mr. Acheson, on the other hand, with more inventive instinct, realized the importance of making his inventions of value to the public. He believed that to discover and to abandon was of little honor, and he never forsook carborundum until he had made it of value to the industrial world.

The actual history of the discovery of this body may be summed up as follows:

As far back as 1849, Gmelin, in his Handbook on Chemistry,

III, p. 359 (Watt's translation), makes an allusion to a carbon-silicon compound, as a somewhat uncertain substance, perhaps represented by the formula CSi.

In or about 1885 Eugene H. and Alfred C. Cowles, while working upon the preparation of an electric furnace for smelting metallic ores, obtained a very hard crystalline body, which appears to have been carbon silicide. They recognized its possible value as an abrasive; but they did not know its composition, and took no steps to follow it up. They were indeed on the point of investigating it, when their furnace and works were destroyed by fire, and the matter was consequently left undetermined. The author had been invited to Lockport to see the supposed artificial sapphire, which was really carborundum.

In 1891 Edward G. Acheson, who had been studying for some time the problem of producing artificial abrasive, began experiments at Monongahela, Pa., with the idea of dissolving carbon in melted silicate of alumina. In an iron vessel he placed a mixture of carbon and clay and caused a powerful electric current to traverse and fuse its center. On breaking open the cooled mass small, bright blue crystals were found surrounding the carbon electrodes. Following up this experiment on a larger scale, with a small brick furnace, the same substance was again produced, and found to be intensely hard, but not carbon. As there was as yet no analysis, Mr. Acheson regarded it as a compound of carbon and alumina, and hence proposed for it the name of carborundum. Further experiments led him to think that the silica present bore an important part in the process and caused him to try a mixture of sand instead of clay, with the carbon, together with a little salt, which had already been found advantageous. These were mixed in the proportion of 40 per cent. each of glass-sand and powdered carbon, from arc lamp-rods, and 20 per cent. of salt. The result was an abundant development of the new substance, crystallized in zones around the carbon core. The alumina was thus shown to have no part in the formation of the compound, and analysis soon revealed its true composition.

The current in these experiments traverses a carbon core in the center of the mass, which is thus subjected to the requisite heat. The mass, on cooling, is found to consist mainly

of a mixture of sand and carbon caked together by the fused salt; within this lies a roughly cylindrical body of slightly varying products surrounding the core in concentric zones. The innermost of these is a mixture of about two-thirds of graphitic carbon and one-third carborundum; then comes the zone of nearly pure carborundum crystals, and outside of this is a thin enveloping zone of a pale greenish color, essentially carbon silicide, but granular, amorphous and soft. This represents the furnace charge at a stage in advance of the formation of the product; while in the innermost zone, immediately around the core, the heat has evidently caused the dissociation of most of the compound, leaving the carbon as graphite.

This, on a greatly enlarged scale, is essentially the process now used in the manufactory of the Corborundum Company at Niagara Falls. Some details have been modified, but nothing very important. It was claimed, however, by the Electric Smelting and Aluminum Company that the process, as conducted here, was an infringement of patents granted in 1885 to the brothers, E. H. and A. C. Cowles, for the construction of an electric furnace of this type; and the first decision in favor of the Carborundum Company, by the United States Circuit Court for the Western District of Pennsylvania, was reversed for the plaintiff by the Court of Appeals of the Third Circuit. It appears that the Messrs. Cowles devised and patented a very similar carborundum incidentally; but not knowing its composition they gave no attention to producing it commercially. The claim of infringement relates not to the product, but to the theory and construction of the furnace.

Mr. Acheson took out a patent in February, 1893,[8] for the "preparation of artificial carbonaceous crystalline materials," and in September of the same year published his article, with the new name, "Carborundum, its History, Manufacture and Uses."[9]

Some months before an article had appeared in Paris by M. Schutzenberger, describing a carbon silicide obtained by him.[10] This, however, was amorphous and quite soft, apparently

[8] U. S. Patent, 492767.

[9] Jour. Franklin Inst., Phila., Sept., 1893. See also William P. Blake, Eng. and Min. Jour., Sept. 9 and 23, 1893.

[10] Compt. Rend., **114**, 1089 (1892), Contributions a l'histoire des composés carbo-siliciques.

identical with the imperfectly formed material in the outer zone of Acheson's furnace product. It had no abrasive value, and can hardly be called carborundum proper, though the same in chemical composition.

It has lately been designated as carbon-silicon, a term which expresses its constitution without confounding it with the hard and valuable crystalline modification.

Professor Moissan's announcement of his discovery appeared soon after that of Acheson.[11] But although he had obtained the compound in 1891, he had made no publication of it, and freely accords the right of priority to Mr. Acheson.[12] Which of the three men named is entitled to rank as the actual first discoverer it is, perhaps, impossible to determine, and the honor may be better shared than disputed.

After ten years' interval this same compound, in minute crystals, was discovered by Professor Moissan, associated with the diamond carbon in the Cañon Diablo iron. As thus a true natural mineral, entitled to a name, it was called by the writer Moissanite, in honor of his eminent friend, the discoverer.[13] The investigation which led to this interesting result will be described further on.

The claim was at first made that this new substance, carborundum, was hard enough to polish the diamond. In order to determine this very important point, the writer and Prof. G. H. Williams made an immediate test of it at the Columbian Exposition at Chicago, in August, 1893.[14] A perfectly new polishing-wheel was first tried upon a diamond, to make sure that the steel contained nothing that could act upon the stone, or could itself affect it any way; and this being proved, it was charged with carborundum and tried for thirty minutes. At the end of this time not the slightest trace or mark had been produced upon the diamond. On the other hand, as soon as a fraction of a milligram of diamond dust was placed on the wheel the well-known cutting sound was observed. This trial showed clearly that

[11] C. R., **116**, 1222 (1893), and especially **117**, 425 (1893), Préparation et propriétés du siliciure de carbone cristallisé.

[12] Le Four Electrique, Moissan, Paris, 1897, pp. 351, 352.

[13] Am. Jour. Sci., **19**, May, 1905.

[14] Am. Jour. Sci. (3), **46**, 471, 472 (Dec., 1893); also Min. Resources of the U. S., 1893, pp. 6-8 (reprint).

carborundum was below 10 in hardness, though much above 9, as it scratches ruby and sapphire freely.

In connection with this experiment another one was made, and described, by Professor Huntington and the writer, upon the supposed diamond particles from the Cañon Diablo iron. A considerable mass of the meteorite was dissolved in acids, and the hard, minute grains of the insoluble residue were tried upon a new wheel in the same way, using the same precautions against any error as those before described. As soon as a milligram of the residue was applied to the wheel the cutting sound was heard, and a polished plane was soon cut upon each of two diamonds. One of these was placed by the writer in the gem collection of the American Museum of Natural History of New York, where it now remains.

As regards carborundum, however, it is exceedingly hard, approaching in this respect the diamond, but not equal to it, as had at first been claimed. No precise value in the hardness-scale has yet been determined for it; all that can be said with certainty being that it is near, but below, 10. Beyond the fact that it will scratch strongly the surface of a ruby or sapphire and not that of a diamond, its hardness is not easy to determine for lack of other bodies whereby to test it. The difference between the units of the Mohs scale of hardness are found to increase greatly in ascending, so that the interval between 9 and 10 is regarded as probably equal to the entire differences from 1 to 9. This general fact was alluded to several years ago by Prof. T. A. Jaggar,[15] of Harvard University, and it has been confirmed more in detail by later experiments conducted at Johns Hopkins University. The hardness of carborundum may, therefore, be far greater than that of sapphire or corundum, while much below that of diamond.

In respect to other physical properties, the carbon silicide is infusible; but at a temperature below that of the electric arc, at about 3400° C., it is dissociated, the silicon being volatilized and the carbon remaining as graphite. It is unaffected by any acids or reagents, even strong hydrofluoric acid producing no action upon it. It is somewhat brittle, in this respect resembling corundum more than diamond.

[15] Am. Jour. Sci. (4), 4, 399 (Dec., 1897), (citing Tschermak, p. 139).

The specific gravity is usually given as 3.12 (Moissan), but it is subject to some variation. Prof. Joseph W. Richards, of Lehigh University,[16] determined one sample as 3.123, in a specific gravity bottle, at 60° F. (25° C.). He also found a difference between the green crystals and the blue, in a Sonstadt solution of 3.2, carefully diluted to 3.05, at which density the green ones had sunk while the blue had not. Dr. Otto Muhlhauser, Mr. Acheson's chemist, found a specific gravity of 3.22[17] for the green crystals, while the Carborundum Company's catalogue gives it as 3.23.

The crystals usually appear as hexagonal plates, but they are strictly rhombohedral, though with a great development of the basal plane, which gives them the former aspect. A full account of the crystallography has been given by the late Prof. B. W. Frazier, of Lehigh University.[18] He determined a number of planes of both direct and inverse rhombohedra, and the prism of the first order, although the basal plane always predominates. These inclined edges can be easily seen on any good crystallized specimen of carborundum. The crystals have a brilliant lustre, and are usually dark green or bronzy with rich, steel-blue reflections. They are generally quite opaque, but in some instances Professor Moissan has obtained them transparent and colorless.[19] He regards the usual coloring as due to small amounts of impurities, particularly iron, the absolutely pure compound being colorless to pale green.[20]

The composition of this body is, theoretically, carbon 30 per cent., and silicon 70, and its formula CSi. Various analyses show a very close approximation to these figures, with slight admixtures of foreign substances. Moissan gives as the result of very exact determinations of the carbon and silicon alone, without considering the minute fraction of impurities, the two following sets of figures[21]:

	I.	II.	Theory.
Silicon	69.70	69.85	70.00
Carbon	30.00	29.80	30.00
	99.70	99.65	100.00

[16] Jour. Franklin Inst., Phila., Sept., 1893, p. 21.
[17] Ibid., p. 17.
[18] Ibid., pp. 19, 20.
[19] Moissan, Le Four Electrique, Paris, 1897, pp. 352, 353.
[20] Catalogue of the Carborundum Company, 1898, p. 11.
[21] Le Four Electrique, p. 355.

Other analyses are given by E. C. Acheson, in his article on carborundum, published in 1893, two of which gave results as follows[22]:

Si	69.19	68.26	
$Al_2O_3 + Fe_2O_3$	0.38	0.77	(Fe_2O_3)
CaO	0.19	0.48	
MgO	0.06		
C	29.71	30.49	
O	0.47		
	100.00	100.00	

Acheson says: "I think Professor Moissan was right in attributing the green color to iron. I think the blue is due to aluminum, and the black to opaque crystals of free carbon in the graphite form. The first crystals I made, using clay, were always blue. If a clean crystal of black color be powdered and thrown into water a scum of graphite appears on the surface of the water. If the powder be washed clean and further pulverized and thrown into water another scum of graphite appears."

Professor Moissan, in his volume on the electric furnace, describes several methods of preparing this compound.[23] One of these is by dissolving carbon in silicon maintained in a state of fusion by means of a blast furnace. On dissolving the silicon in a mixture of nitric and hydrofluoric acids handsome crystals of the carbon silicide, several millimeters in length, are set free. The temperature of the fused silicon, in which the crystals are thus readily formed, is between 1200° and 1400° C.

Using the electric furnace, a mixture of 12 parts of carbon and 28 of silicon is simply heated, and a mass of crystals is readily produced, and afterwards treated with acids, etc., to remove any uncombined residue. The crystals from this process are generally yellow, but may be transparent and sapphire-blue. A third process is by obtaining the compound from silicide of iron, and more simply from a mixture of iron, silicon and carbon (or charcoal). This method produces the deeply colored crystals.

Still another mode of forming carborundum is by the reduction of silica by carbon in a crucible in the electric furnace. The crystals thus obtained, M. Moissan observes, are less colored

[22] Jour. Franklin Inst., Phila., Sept., 1893, pp. 6 and 8.

[23] Le Four Electrique, pp. 352, 353.

than those formed by the preceding method, showing that the iron is the main source of the strong coloration.

One more process is described, in which the two elements are both vaporized and allowed to react on each other, a small carbon crucible containing a regulus of silicon being raised to a very high temperature. On cooling, needle-like prismatic crystals of carbon silicide are found, which are nearly colorless, brittle and very hard.

Carborundum is now manufactured on an extensive scale in the great works of the Carborundum Company at Niagara Falls, N. Y., where the power for the electric furnaces is derived from the falls. E. C. Acheson, the first describer of the new compound, organized this company; and the process is that developed by him in his early investigations, with but slight changes. The furnaces are very simple in construction, consisting of oblong boxes or stacks of brick, about 17 feet long by 6 feet wide and high, laid up without morter or cement. At each end a bronze plate is attached, connecting outside with copper cables and rods carrying the current, and inside with sixty carbon rods or bars, three inches in diameter, which extend into the furnace and form the terminals. The interior of the stack is then filled with a mixture of pure silicious sand, powdered coke from Pennsylvania bituminous coal, salt from the works near Syracuse, N. Y., and saw-dust. A sort of core of the granulated coke is moulded so as to extend through this mass between the terminals. The current is then turned on after being reduced to about 180 volts by a transformer, and allowed to pass for 24 to 36 hours. Gases escape through the uncemented brickwork, enveloping the furnaces in blue and yellow flames. When the current is cut off the bricks are taken down and the interior mass exposed. The salt has been volatilized and the saw-dust burned; the rest of the mass is loosely caked around the core, about which the carborundum has formed as a surrounding zone of a foot or more in diameter of brilliant crystals radially disposed. Within this zone the core itself has been materially altered—the hard, lustrous coke having been changed into a softer, dull-black mass of mixed unctuous and non-unctuous graphite. At the junction of this altered core with the surrounding carborundum is sometimes found a very interesting substance, viz.: a layer

of dull-black crystals, having the form of carborundum, but consisting of pure graphite. These, which Mr. Acheson has called "the carbon skeleton of carborundum," represent crystals of the latter that have been dissociated by the heat, after their formation, the silicon having been volatilized and only the carbon left.

An interesting suggestion is afforded by this circumstance as to the alteration of amorphous carbon into graphite. This has usually been supposed to be due to heat alone; but Mr. Acheson inclines to the view that there is first a combination of the carbon with various impurities present therein in small amounts; that these compounds are then dissociated, as the heat continues and increases, and that the graphite is the final result, as it plainly is in these residual "skeletons" of carborundum.[24]

On the other hand, the recent article of F. A. J. FitzGerald, on "The Use of Carbon for the Study of Temperatures in the Electric Furnace,"[25] and the experiments described therein on the conversion of carbon into graphite by heat alone, seem to show that this latter is a normal and sufficient method, although the view of Acheson may be correct in certain special conditions.

Carborundum and Other Carbides.

The industrial importance of carborundum as an abrasive next only to the diamond, and the remarkable discoveries and experiments of Moissan and others in the production of a large body of similar carbides new to science, by means of the electric furnace, have led to a considerable literature on the whole subject. This was collated and indexed by J. A. Mathews, in a pamphlet published by the Smithsonian Institution.[26]

Over thirty carbides are noted in this paper, with their mode of preparation, leading properties and bibliography. Reference may be made here only to a few that present features of possible importance, such as great hardness, in ways similar to carborundum; though, as yet, no others appear to have been so utilized. A compound of aluminum, boron and carbon, expressed by $Al_3C_2B_{48}$, is referred to as possessing extreme hardness, between corundum

[24] The Carborundum Co., Catalogue No. 4, 1903, pp. 14, 15.

[25] Sixth Gen. Meeting Amer. Electrochemical Society, St. Louis, Sept., 1904, pp. 31-37.

[26] Smiths. Misc. Coll., No. 1090, Vol. XXXVIII—Review and Bibliography of the Metallic Carbides, 1898.

and diamond; but the notice is brief and the substance is little known. The reference goes back to Hampe in Ann. Chem. for 1876. Moissan has formed a boron carbide, B_6C, in bright black crystals, said to be harder than carborundum, with which faces may be cut upon diamond. Another boron carbide, BC or B_2C_2, is not so hard and fuses at a high heat. The chromium, uranium, vanadium and zirconium carbides are all harder than quartz; and several others are spoken of as "very hard," but without specifying further.

Artificial Diamonds.

At about the same time, Professor Moissan was devising and conducting his notable experiments on the artificial production of diamond by means of the electric furnace. His general process is now well known and need not be re-described here. Moissan introduced carbon into a regulus of iron, fused and then cooled under enormous pressure; he made some 300 experiments, and believed that he thus produced true diamonds in each and every instance. He obtained several hundred crystals, but so minute that the diamonds formed in all the experiments amounted to only about half a carat—100 milligrams, or 1/300 of an ounce—to an experiment; while their actual cost was nearly 10,000 francs, or 2,000 times the value of natural diamond powder. Commercially, therefore, his results were valueless, but scientifically they have great interest. Among the diamonds thus produced he found three types: (1) transparent and crystalline, some of them octahedral and some round and drop-like; (2) transparent, with tiny black carbon specks, which he terms *diamants a crapauds;* and (3) the amorphous form known as black diamond or carbonado, which he calls "diamants noirs."

All these experiments and results are fully described and figured in Professor Moissan's important work, "Le Four Electrique," published in 1897; but his first published announcements were made in 1893.[27]

On his visit to this country, in 1896, he lectured before the leading scientific societies of New York, at the College of Physicians and Surgeons. On this occasion he performed his won-

[27] Comptes Rendus, **116**, 218 (1893), and especially **118**, 320 (1894), Nouvelles expériences sur la réproduction du diamant.

derful experiments in the artificial production of diamonds with such ease, confidence and beauty as to leave an abiding impression. Who that witnessed it can forget the striking scene? As Moissan, with his noble black beard and hair, stood facing the audience, he laid his hand fully and firmly on the lime cover of the glowing electric furnace—knowing that it could not injure his hand—then raised the cover, and taking the crucible from the furnace, he plunged it directly into water, not heeding the violent sputtering and steam produced by the contact, and in a tone of quiet confidence remarked: "I know that this regulus contains diamonds, because in the 300 experiments that I have made there has *never* been a failure." That scene would have made a fit subject for a great painting, to be entitled "The Triumphant Chemist"—one worthy to stand as a companion and a contrast to that called "The Doubtful Alchemist."

These results attracted world-wide attention, and were taken up especially by Sir William Crookes, who successfully repeated the experiments in lectures in England, and who applied the idea of some such origin, in masses of heated iron at great depths, to the production of diamonds in nature, especially in the great South African mines. A noted lecture before the Royal Institution, London, in which Doctor Crookes presented these views, together with many other important points relating to diamond and the several forms of carbon, was republished in the Report of the Smithsonian Institution for 1897, pp. 219-235.[28]

Dr. Moissan had long given a great deal of study to the diamond and all the forms of carbon found in nature or producible by any artificial methods. The list of his papers on these subjects is very extensive, and comprises researches on the blue-ground of South Africa[29]; on the diamond-sands of Brazil[30]; on carbonado[31]; on the vaporization of carbon[32]; on several varieties of graphite[33]; on the solubility of carbon in various

[28] Jour. Royal Inst., **5** (1897); also Nature, **56**, 325-331 (Aug. 5, 1897). See also abstract in Min. Res. U. S. (19th Ann. Rep. U. S. G. S.), 1897.

[29] Compt. Rend., **116**, 292 (1893), Sur la presence du graphite, du carbonado et de diamants microscopiques dans la terre bleue du Cap.

[30] Compt. Rend., **123**, 277 (1896), Études des sables diamantiféres du Brésil.

[31] Compt. Rend., **121**, 449 (1895), Sur un échantillon de carbon noir de Brésil, and also **123**, 210 (1896), Étude du diamant noir.

[32] C. R., **119**, 776 (1894), Sur la vaporisation du carbone.

[33] C. R., **116**, 460 (1893), Sur la préparation d'une variété de graphite foissannante, and **120**, 17 (1895), Préparation du four électrique de graphites foissannantes; also C. R., **119**, 776 (1894), Études des differentes variétés de graphite, and p. 1245, Études des graphites du fer; also C. R., **121**, 538 (1895), Étude de graphite extrait d'une pegmatite, and p. 540, Étude de quelques variétés de graphite.

metals,[34] and a number of related topics[35], to say nothing of his production of the new and remarkable series of carbides of the metals. Very naturally, he also paid much attention to meteorites, in their relation to products of the electric furnace and to the occurrences of carbon in some of them, beginning with that of Cañon Diablo,[36] and he published several papers giving his observations and deductions.[37]

It is highly interesting to trace the connection between these various investigations, and also the manner in which they influenced the mind of Professor Moissan, and led him on to his ultimate achievement in diamond production. His historical and logical progress in his researches and experiments, though not formally stated, appears very strikingly in a lecture given by him in August, 1893, before the "Societe des Amis des Sciences."[38] After describing on this occasion the properties of diamond and its relation to the other forms of carbon, and showing the alteration of a diamond to graphite between the poles of the electric arc, he proceeded to the consideration of the diamond mines of South Africa, and to his examination of the "blue-ground" and the minerals contained in it, associated with the diamonds. In the study of these minerals he cordially recognized the co-operation of M. Stanislaus Meunier. The point emphasized was the

[34] C. R., **123**, 16 (1895), Sur la solubilité du carbone dans le rhodium, l'iridium, et le palladium.

[35] C. R., **116**, 218 (1893), Sur la préparation du carbone sous une forte pression; ib., p. 458, Analyse des cendres du diamant; and p. 460, Sur quelques propriétés nouvelles du diamant, and **117**, 423, Action de l'arc électrique sur le diamant, etc.; also C. R., **123**, 206 (1895), Sur quelques expériences relatives a la préparation du diamant (his noted experiments), and Annales de chimie et de physiques, 7° serie, 8 (1896), pp. 289, 306, and 466 (three memoirs), Recherches sur les différentes variétés de carbone.

See also Comptes Rendus:

124 (1897), p. 653, Sur le transformation du diamant en graphite dans le tube de Crookes.

Ib., p. 716, Préparation du carbure de fer par union directe du métal et du carbone.

126 (1898), p. 302, Sur les conditions de formation des carbures alcalins, des carbures alcalino-terreux, and du carbure de magnesium.

127 (1898), p. 457, Analyse de quelques échantillons industriels de carbure de calcium.

Ib., p. 917, Sur la couleur de carbure de calcium.

131 (1900), p. 595, Préparation and propriétés des carbures de néodyme and praséodyme.

Ib., p. 924, Étude du carbure de samarium.

135 (1902), p. 921, Sur la température d'inflammation and sur la combustion dans l'oxygéne, des trois variétés de carbone.

137 (1903), p. 292, Sur un carbure double de chrome et de tungstene.

[36] C. R., **116**, 288 (1893), Étude de la météorite de Cañon Diablo.

[37] Ib., p. 1269, Sur le fer d'Ovifak, and **121**, p. 483 (1895), sur quelques météorites. (The full list of Prof. Moissan's papers up to 1896, is given in his work, "Le Four Electrique," pp. 374-376.)

[38] Révue Sciéntifique, **52**, No. 7 (1893), pp. 193-200.

large proportion of iron minerals among those thus determined. He then tells how he proceeded to burn diamonds and analyze their ash, and found iron as a constant ingredient therein, sometimes in large proportion. He was thus led to the view that the Cape diamonds and the associated graphite must have crystallized out from solution in melted iron; and hence he undertook extended studies on the solubility of carbon in iron and other metals. It was largely in the course of these experiments, with the aid of the electric furnace, that his notable series of results was attained in the preparation of rare and refractory elements in a pure state, and in the production of the new and remarkable body of metallic carbides that have made his fame permanent. Still, with many important results, and with constant improvements in the adjustments of the furnace, he failed to obtain diamonds from iron—the carbon always separating in the form of graphite. It was at this period in his studies that the discovery of microscopic diamonds in the Cañon Diablo meteorite, by Koenig, in 1891, was announced, and was subsequently confirmed by his own examination, as above noted. This discovery led to further attempts to reproduce the natural conditions. Gradually he reached the conclusion that besides solution in the metal at very high temperatures, enormous pressure must be a necessary condition for crystallizing the carbon as diamond—the dense variety. The analogous case of the transformations of phosphorus under great pressure, by Troost and Hautefeuille, afforded a precedent. In studying how to bring about such a condition with carbon in molten iron, Moissan finally conceived his method of suddenly cooling the exterior of the crucible by immersion in water, and thereby compelling the interior mass to solidify under the immense pressure of its own tendency to expand, prevented by the solidification of the outside as a confining envelope. At last the problem was solved and the goal attained! And the dissolved carbon appeared as minute crystals of actual diamond.

This remarkable achievement of Professor Moissan has not led to any commercial results, as the diamond crystals thus obtained are extremely minute. But it has great scientific interest, especially in relation with the occurrence of diamond carbon in meteorites. Professor Rossel, of the University of Berne, has gone a step further and made an investigation as to the possible

presence of diamond carbon in very hard steels and in some extremely tough varieties of iron from the bottom of blast furnaces, where the pressure is very great.[39] The result proved the correctness of this suggestion, as Professor Rossel obtained from such sources minute particles having octahedral crystallization and presenting all the physical properties of diamond. The largest of these do not exceed half a millimeter in diameter.

Such was the general course of these connected researches, in which diamond and other forms of carbon, high temperature compounds of silicon, carbon and other refractory elements, and meteoric irons and their contents, all entered as starting points, steps or results. All these were fully described in Professor Moissan's great volume, the comprehensive history of his life-work, published in Paris in 1897, under the title of "Le Four Electrique."[40]

On subsequently examining a portion of the celebrated Cañon Diablo metorite in his own laboratory, Professor Moissan used a mass of the iron weighing 183 kilograms; and the first step was to cut it up by means of a steel ribbon saw, operated by steam. Very soon, the first experiences of Foote and Koenig, in 1891, were repeated, the saw encountering very hard portions that obstructed its course. No less than twenty days were required to divide the mass into two parts, with a section area of about 625 square centimeters. The obstacles were then seen to be round or elliptical portions, afterwards proved to be nodules, from one to two or three centimeters in diameter, of dark grey to black color, enclosed in the bright iron. Some of them had a black exterior coating. The iron and the nodules were separately studied; and it then appeared that the meteorite was not homogeneous, the percentage of nickel varying in different portions of the mass from 1.66 to 3.61. It also contained, as a whole, a little phosphorus, silicon, carbon, sulphur, magnesium and traces of cobalt (not before recognized). The carbon and phosphorus were richest in the vicinity of the nodules.

The nodules, consisting mainly of troilite (iron protosulphide), were treated with hydrochloric acid, releasing much hydrogen sulphide, and dissolving a considerable amount of iron, some

[39] Journal Officiel Illustre de l'Exposition Nationale Suisse, 1896, No. 40, p. 477.

[40] Le Four Electrique, Paris, G. Steinheil, 1897, 8vo, pp. vi, 385.

nickel, traces of cobalt, and a little phosphorus, sulphur, carbon and magnesium. The iron and phosphorus probably existed in combination as a phosphide of iron, apparently Fe_3P_2. The insoluble residue contained silica, amorphous carbon, graphite and diamonds, both black and transparent, the latter as minute octahedrons with rounded edges. The black diamonds were abundant, but very small. But the most novel result of this examination was the discovery of carbon silicide (carborundum) for the first time as a natural mineral, in small, green hexagonal crystals, of characteristic type. These were found, with the carbon, etc., in the insoluble residue of the nodules.

A number of interesting and curious problems begin to arise from these various observations and experiments, as to the former conditions existing in meteorites; the genesis of carbon silicide and the different varieties of carbon found in them; the existence of similar conditions in the earth's interior; and the origin of diamonds and carbon compounds in deep-seated rocks. To go into these discussions would far exceed the possible limits of such a notice as the present, but a few points may be briefly noted.

(1) As to temperature. It is well known that carborundum is dissociated at high temperatures, the silicon being volatilized and the carbon left behind as graphite. The volatization of silicon by the electric furnace was one of Moissan's remarkable achievements, the silicon in that case being reduced from silica by carbon. The temperature at which carbon silicide is dissociated is said to be about 3400° C.

Crookes has emphasized the fact that diamond is converted into graphite by heat, or by molecular bombardment in a Crookes tube.[41] The latter treatment produces on a diamond an exterior coating of graphite, which Moissan has shown must have required a temperature of about 3600° C.[42] Dewar, as far back as 1880, converted a diamond into graphite by the heat of the electric arc in a current of hydrogen gas in a carbon tube.[43] Crookes repeated this experiment in his Victorian Jubilée lecture, before referred to, changing a clear diamond crystal into very hard graphite in a few minutes by the electric arc at a temperature of

[41] Chem. News, **74**, 39 (1896).

[42] Compt. Rend., **114**, 658.

[43] Proc. Royal Inst., Jan. 16, 1880.

3600° C.,[44] as did also Moissan in his address in 1893, also noted above.[45]

The presence of carbon in certain meteorites, in the form of what seem to be pseudomorphs of diamond in graphite, becomes very suggestive in view of these and similar observations. The cliftonite of Fletcher,[46] from the Youndegin (Australia) meteorite, and the isometric graphite crystals in the Arva (Hungary) meteorite,[47] both previously mentioned, are presumably such alterations. At the same time, it is fair to say that some writers, such as J. M. Davison,[48] are inclined to regard these as peculiar types of hard graphite, independently produced under special conditions.

Do these data furnish clues to the temperature of meteorites within which these different bodies have been formed? If carbon silicide cannot exist above 3400° C., and carbon in the diamond form is altered to graphite at 3600°C., it would seem that these temperatures must mark the lower and upper limits of diamond occurrence in meteorites. If so, the same reasoning may extend to conditions in the earth's interior, on the Crookes-Moissan theory of an analogous source of terrestrial diamonds in masses of fused iron. Moreover, there would appear to follow the conception of different temperatures in different meteorites, and at different times in the history of the same meteorite, with the indication in some of them at least, of increasing temperatures, in which carbon silicide, diamonds and graphitized diamonds may have been successively formed. In this view, the Cañon Diablo iron, in which carbon silicide yet remains, and true diamonds are present, would appear never to have reached a temperature such as the Arva and Youndegin meteorites have.

(2) As to oxygen. It seems very clear, also, that such meteorites must have formed, and existed for most of their history, in regions where oxygen was absent. Neither carbon itself, in any of its forms, nor carbon silicide, could develop in the presence of free oxygen; carbonic and silicic acids would inevitably

[44] Proc. Royal Inst., June 11, 1897; Nature, **56**, No. 1449, Aug. 5, 1897; Smith's Rep., 1897, p. 225.

[45] Révue Sciéntifique, **52**, No. 7, 1893, pp. 194, 195.

[46] Miner. Mag., London, **7**, 121, 1887.

[47] Dana, Syst. Min., 6th Ed., 1892, p. 7.

[48] Am. J. Sci. (4), **13**, June, 1902, and Min. Res. U. S., 1892, pp. 30, 32 (reprint).

be produced under such conditions. Hence, wherever these wandering siderites took shape and passed through their formative stages, oxygen must have been absent. This suggestion leads at once to interesting problems as to the formation of such bodies in regions of the universe widely different in conditions; the iron and carbon meteorites requiring an environment wholly distinct from those in which silicates, such as olivine, enstatite, and the like, are freely developed.

There is no question that most meteorites and aërolites have fallen to the earth from space; but in regard to some of them, especially certain very large masses, there is a difference of opinion among students of the subject, some holding to the view that they may have been ejected from the interior of the earth. Formerly it was believed that the nickeliferous iron, with its extreme toughness and its characteristic Widmanstätten markings, was in all cases derived from space; but the discovery of the Ovifak iron in Greenland, possessing all these meteoric characters, and yet an undoubted outcrop, made this view untenable. It thus appeared that the same material as forms the siderite meteorites may and does exist in or beneath the earth's crust.

The view has been taken by some eminent authorities, especially Prof. G. K. Gilbert, that the Cañon Diablo irons may represent, not a fall, but an ejection.

Under most circumstances on the earth's surface, iron oxidizes so rapidly that pieces of it exposed to the atmosphere must sooner or later disappear. The nickel of meteoric irons would seem to exert a strong influence in retarding this process, but can scarcely prevent it. The point may be noted, however, that it is largely a question of moisture; and that if either by aridity, as in Arizona, or by cold, as in high latitudes, the action of moisture is prevented or greatly limited, iron may remain long unoxidized even upon the surface of the ground. It is a fact that iron or steel, if kept in a temperature below the freezing point, in snow or even in water, does not rust, or only very slightly.

Hence, in the finding either of meteorites or of great masses of terrestrial iron in the vicinity of the Arctic Circle, their presence can be explained by this fact, as at Ovifak the temperature is never above zero degrees during th entire year. Hence, a

mass of meteoric iron, or even grains of iron in a basaltic rock, as at Ovifak, would not be liable to oxidize. This may well explain such occurrences in arctic regions; while in so dry a country as that around Cañon Diablo, the same result may be brought about by a different cause. These considerations are suggested as of possible value, although they cannot apply in all cases where large masses of iron, presumably meteoric, have been found, such as the great pieces lately discovered in Mexico and the State of Washington, the former first described by Prof. H. A. Ward, and the latter by the writer and subsequently by Doctor Ward.

There has been much dispute among chemists as to the precise nature of the familiar process known as rusting; some holding that oxygen cannot or does not attack iron in the absence of moisture or of carbon dioxide, and the subject has been quite actively discussed of late. Whatever the result may be, however, the argument here presented in regard to cold is unaffected, and the presence of moisture is unquestionably a very important condition of rusting, even if not absolutely necessary.

In his latest study of the Cañon Diablo iron, Professor Moissan had found, as above noted, that the carbon was present in and around the nodules of troilite, and in certain minute fissures that seemed to connect them, and also in close association with carbon silicide (moissanite) and apparently an iron phosphide in minute amounts. These observations, together with experiments by Stead and others, which are specially cited, led him to the view that the presence of sulphur, phosphorus or silicon in a molten iron may tend to favor the separation of carbon therefrom; while the nickel present in meteoric iron lessens the solubility of carbon in the alloy thus formed. He concludes his article with the following words: "These two phenomena have combined to separate the carbon from what must have been a liquid condition when carbon silicide was formed. Later, we propose to study the influence of pressure on these various reactions.[49]

Professor Moissan was unable to fulfill this purpose during the following year (1905), and presented the results of his further study in an article entitled, "New Experiments on the Prepara-

[49] Compt. Rend., **139**, No. 20, Nov. 14, 1904, and Chem. News, **90**, No. 2351, Dec. 16, 1904 (abstr. and transl.).

tion of Diamonds."[50] After referring to his former researches on diamond-production (Ann. de Ch. et de Phys., viii, pp. 289, 306, 466), and to the successful repetition of them by Sir William Crookes (Proc. Royal Inst., XV, p. 477), and by some others, and recurring to his observations on the Cañon Diablo meteorite and his belief that the non-metals above noted had favored the separation of the carbon in crystalline form, he described his further experiments. These were directed toward determining the question whether sulphur, phosphorus or silicon has any decided influence in separating diamond carbon, and how far pressure is involved in the result. The first experiments related to the effect of sulphur, without pressure, and then with pressure.

For this purpose 150 grms. of Swedish iron, broken into fragments of a few c.c. each, were melted in the electric furnace in presence of sugar carbon. The saturation of the iron with carbon at the temperature of the electric furnace is completed in two or three minutes with a current of 400 amperes under 120 volts pressure. The crucible containing the liquid iron is removed from the furnace, and a solid fragment of iron mono-sulphide of about 5 grms. added, which melts and mixes with the mass. The metal swells, and gases are evolved in abundance. After cooling, the metallic mass is treated with acids in the usual manner. The graphite is transformed into graphitic oxide, then into pyrographitic oxide, and this latter compound is destroyed by a mixture of boiling sulphuric acid, into which is thrown about 5 grms. of potassium nitrate—a small quantity at a time. After alternate treatments of this residue with hydrofluoric and sulphuric acids and then fusion with fluohydrate of potassium, it is decanted, dried and tested with methylene iodide of density 3.4, and the portion falling to the bottom is collected. Under these conditions no diamonds were found, all the carbon appearing as graphite.

The same process was then repeated, but the crucible was cooled suddenly on the outside by immersion in cold water, as in Professor Moissan's former experiments when he produced microscopic diamonds. The contrast of results was striking. Professor Moissan says:

"The porous graphite vessel is rapidly penetrated by the water,

[50] C. R., **140**, No. 5, p. 277, and abstr. and transl. in Chem. News, **91**, No. 2361, Feb. 24, 1905.

and the metallic mass is cooled externally, forming a solid crust. Under these conditions an internal pressure is produced, and the carbon which is deposited from the still liquid central part takes the form of diamonds. The appearance of the metallic ingots to which the sulphur is added is naturally somewhat different from the iron ingots ordinarily cooled in water. There is a similar external resisting portion, but the upper surface of the metal, if the melt and the iron sulphide are rapidly cooled, is covered with a black, solid, spongy-looking mass, proving the rapid solidification of the emulsionized metal during a brisk gaseous evolution. If the gas had time to be evolved before immersion in water the ingot presents a normal appearance. The diamonds which I obtained by this addition of iron sulphide are of the same form as those formerly prepared. They have the appearance of drops with octahedral ends, composed of superposed layers with curved faces. I obtained several of these octahedra, the different crystals being mounted in Canada balsam and placed between two glass plates. Some of these specimens I presented to the Académie."

The diamonds obtained in this experiment were found to burn away on platinum foil, leaving no ash, *i. e.,* oxidizing to carbonic acid gas. Professor Moissan says that the only difference observed from his previous experiments was that the yield in this case, when sulphur was present, was "distinctly higher than any previously obtained. In a single ingot I have collected eight to ten little diamonds, of which half or two-thirds could be separated with a steel needle without a magnifying glass."

The next step was to try the effect of a small admixture of silicon. This was tested in a number of experiments—either melted silicon or carbon silicide being added to the iron saturated with carbon at the temperature of the electric furnace, previous to the rapid cooling in water. Professor Moissan gives the result as follows:

"In this case diamonds were also obtained, and I think the yield was greater than that in the previous experiments described. But the large quantity of carbon silicide produced, especially when melted silicon is employed, renders the separation by means of methylene iodide much more difficult.

"The carbon silicide prepared in the iron is always blue or green, as was shown in 1893, and so it is impossible, if we examine the silicide under the microscope, to confuse these with the black or transparent diamond fragments. Besides, the density being only 3.12, they float on the surface of methylene iodide.

"Diamonds prepared with silicon have a more irregular form than those prepared by the former method. There are also a large proportion of flawed and black diamonds. Under these conditions I also obtained a large number of diamonds having square surface impressions. The extremities of some were terminated by chapelets of pillared cubes. Some of the diamonds which cracked some weeks and even some months after their preparation, showed the fissures covered with minute cubes. By this preparation the drop form is rarer and there are no octahedra. The yield is also a little higher than that obtained in my experiment of 1893. In several cases I separated 10 to 15 microscopic diamonds from a single ingot. The larger of these are about 0.75 mm. long, the octahedra being 0.2 mm., and many of the drops being 0.4 to 0.1 mm. long."

These diamonds are of the same order of magnitude as those which were extracted from the Cañon Diablo meteorite, some of them being even a little larger. They are all, however, practically microscopic particles.

Two series of experiments made under the same conditions with iron phosphide gave no diamonds, thus indicating that while silicon and sulphur appear to favor the crystallization of contained carbon from iron in the diamond form, phosphorus has no such effect.

The remainder of Professor Moissan's article was given to various observations on the crystallographic and optical properties of these artificial diamond grains, particularly their characteristic greasy luster, also their slight and variable double refraction shown with polarized light. This feature in diamonds and other isometric crystals is well known and has been generally recognized as due to strains from pressure.

Professor Moissan concludes his account by saying: "The new experiments which I have here published as a continuation of my investigations of the Cañon Diablo meteorite, merely corroborate my previous researches. I have always regarded the

diamond as that variety of carbon which had been liquefied under a great pressure, while I proved a long time ago that at ordinary pressure all specimens of carbon under the action of a very high temperature vaporize without passing into the liquid state, and always yield the same variety of carbon—namely, graphite."[51]

In connection with these observations of Professor Moissan, it is of interest to note that a small book has recently appeared abroad, by an American writer, Mr. Francis A. J. Fitz-Gerald, on artificial graphite made in the electric furnace, which is regarded as a very complete and accurate account, and a just matter of pride to American electro-chemists. The work forms "Band XV" of a series of monographs on these subjects published in Germany by W. Knapp.[52]

The widespread interest in regard to the origin and possible production of diamonds, arising from Professor Moissan's discoveries, has led to a great many attempts and professions, some of them visionary and others fraudulent.

New processes for making diamonds artificially are continually being announced, not only in the daily press, but also in high places; notably, the case of M. Charette, who during the past three months has exhibited what purported to be artificial diamonds before the French Academy of Sciences. A committee appointed to investigate them found that they were crystals of naphthaline and not diamonds.

During the past month a great financial magnate is said to have invested over £60,000 in a process for making diamonds, only to find that the supposed inventor was more expert in sleight of hand than he was in chemical processes.

During the past week a great gun-maker has also encountered an invention of this character, but with what success there is nothing definite to say.

Personally, I have known instances where the supposed diamonds proved to be crystals of salt, crystals of sugar, or grains of quartz, and in some cases they were later on admitted by the people themselves to be natural diamonds which they had bought in the market.

[51] Comptes Rendus, **140**, No. 5, p. 277.

[52] Künstlicher Graphit, Halle A. S., Wilhelm Knapp, 1904, pp. 60.

A paper read by F. S. MacGregor at the Twelfth General Meeting of The American Electrochemical Society, in New City, October 18, 1907; President C. F. Burgess in the chair.

ON THE ELECTROTHERMIC REDUCTION OF IRON ORES.

By Albert E. Greene and Frank S. MacGregor.

Investigations up to the present time have demonstrated that iron ore can be economically smelted in the electric furnace where power is cheap; they have shown that the electric furnace does not differ essentially from the blast furnace, from the metallurgical point of view, and furthermore, that it has certain advantages in the regulation of temperature and localization of heat which make it especially applicable for smelting refractory ores and for making special varieties of pig iron.

There are many phases of the problem of smelting iron in the electric furnace regarding which data are entirely lacking at the present time, and this paper contains the results of an experimental investigation which we carried out in the electrochemical laboratory of the Massachusetts Institute of Technology.

The points to which we particularly directed our attention were:

1. The design and construction of an experimental electric furnace of about 30 kw. capacity.
2. The measurement of the temperature of the molten charge.
3. The factors affecting the temperature and the methods of regulating it.
4. The effect of temperature on the quality of the iron produced, and of composition of the charge.
5. The calculation of the amount of electrical energy required per ton of pig iron.

In planning our investigation, it was necessary to start out with very little data regarding the best size and shape of the furnace, the character of the materials to be used, and the details of the application of the power, etc. We first built the furnace, making its size and shape conform to the power at our disposal, then made preliminary runs with one of the Pacific Coast sands,

of which we had a considerable amount. We thus obtained a working knowledge of the method of measuring the temperature, etc., after which we made runs in which first the temperature was varied, keeping the charge constant; and second, the charge itself was varied.

We obtained three samples of ore with which to carry out the investigation. Two of these were iron sands from the Pacific Coast, and the third was a titanium iron ore from Essex County, New York.

Six preliminary runs, designed to test the best method of operating the furnace and measuring the temperature, did not lead to conclusive results concerning their own possible value as a source of iron. The ore upon which the results of our investigation are based consists largely of ilmenite, with practically no sulphur or phosphorus.

Its analysis is

Fe_2O_3	70.40	per cent.
SiO_2	1.99	" "
TiO_2	26.40	" "
Al_2O_3	small amount	
MnO_2	small amount	
Total iron	52.52	per cent.

We crushed it to about ¼ inch, in preparation for the furnace. We used the best grade of Pocahontas coke as a reducing agent and the flux was burnt lime, being almost pure CaO.

We used alternating current for our experiments, and it was generated in a special 1,100-volt, 133-cycle, 50 horse-power generator, belt-driven by a 50 horse-power direct-current motor, supplied with power from the plant of the Institute. The current was transmitted at 1,100 volts to the transformer in the furnace laboratory, from which it could be taken at voltages varying from 10 to 160 volts, and applied directly to the furnace. We measured the temperature of the molten charge by means of a Wanner optical pyrometer, reading from 0° to 4000° C.

We first constructed the furnace as follows: A plate of iron ¾ inch thick was cast in the form of a rectangle, 28 x 24 inches. A 4 x 6-inch tongue projected at one corner, to which the electrical cables were fastened. We then bored five

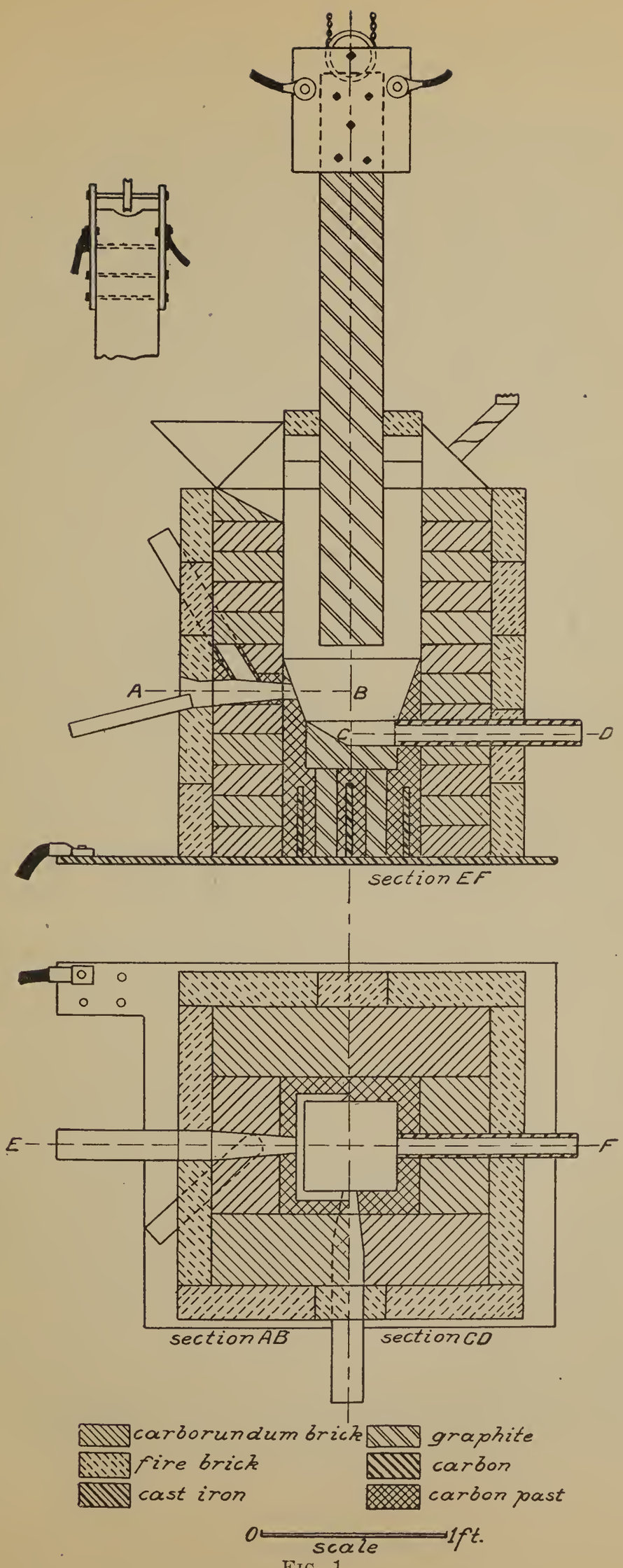

A
B
C
D
section EF
E
F
section AB
section CD
carborundum brick
graphite
fire brick
carbon
cast iron
carbon past
0
1ft.
scale

FIG. 1.

holes, 5/8 inch in diameter and 2¼ inches apart, in the center portion of the plate. Into each of these was firmly driven an iron rod, 8 inches long, to aid the conduction of the current from the bed plate into the crucible, which was to act as one electrode.

Carborundum bricks were laid in thin cement around the rods, forming an enclosure 9 inches square and 9 inches deep. This space was filled with a mixture of granular coke and molasses, and the crucible formed above of this same material. Carborundum bricks were used to complete the crucible, around which a layer of fire-bricks was then placed, forming the outside of the furnace. A tap-hole for metal was placed on one side of the furnace, and on an adjacent side, about 2 inches above the metal tap-hole, was placed a tap-hole for slag. We used conical carbon rods as plugs during the runs. The other electrode was made movable, and consisted of a graphite bar 4 inches square by 40 inches long. The holder consisted of two brass plates, bolted to opposite sides of the electrode by bolts running through the electrode itself. The plates projected above the end of the electrode, so as to form a support for a grooved pulley. An iron chain fastened to a crane gave an easy adjustment of the electrode, which could either be lowered to the bottom of the crucible or hoisted above the top. Four flexible copper cables were bolted to the supporting plates, giving the electrical connection.

On one side of the top of the furnace we placed a hopper for holding a charge, and the rest of the top was enclosed. The information we obtained from the first six runs caused us to introduce various changes in the crucible, and, after many materials were used (such as coke and brasque, original ore and coke, etc., all mixed with molasses), a lining of flour, carbon, and molasses was found to give the most permanent lining.

The shape of the crucible was that of a frustum of a pyramid, the sloping walls extending upward about 8 inches, the rest of the wall being carborundum bricks. The dimensions of the furnace and crucible as finally used are as follows:

Height of furnace	2 ft.
Length of side	1 ft. 11 in.
Depth of crucible proper	8 in.
Size of upper portion of crucible	9 in. sq.
Distance from bottom of crucible to top of furnace	1 ft. 3¼ in.

We did much experimenting in the development of a suitable method for obtaining the temperature of the molten charge while keeping the top of the furnace closed. This was necessary, as we intended to get the temperature, volume and composition of the gases given off during the smelting of the charges, and therefore must have had no openings at the top.

In the first runs, the pyrometer was sighted through a carbon tube, 1 inch internal diameter and 12 inches long, which was introduced diagonally downward through the furnace from the outside into the molten charge. We were obliged to abandon this, as the molten slag solidified in the tube.

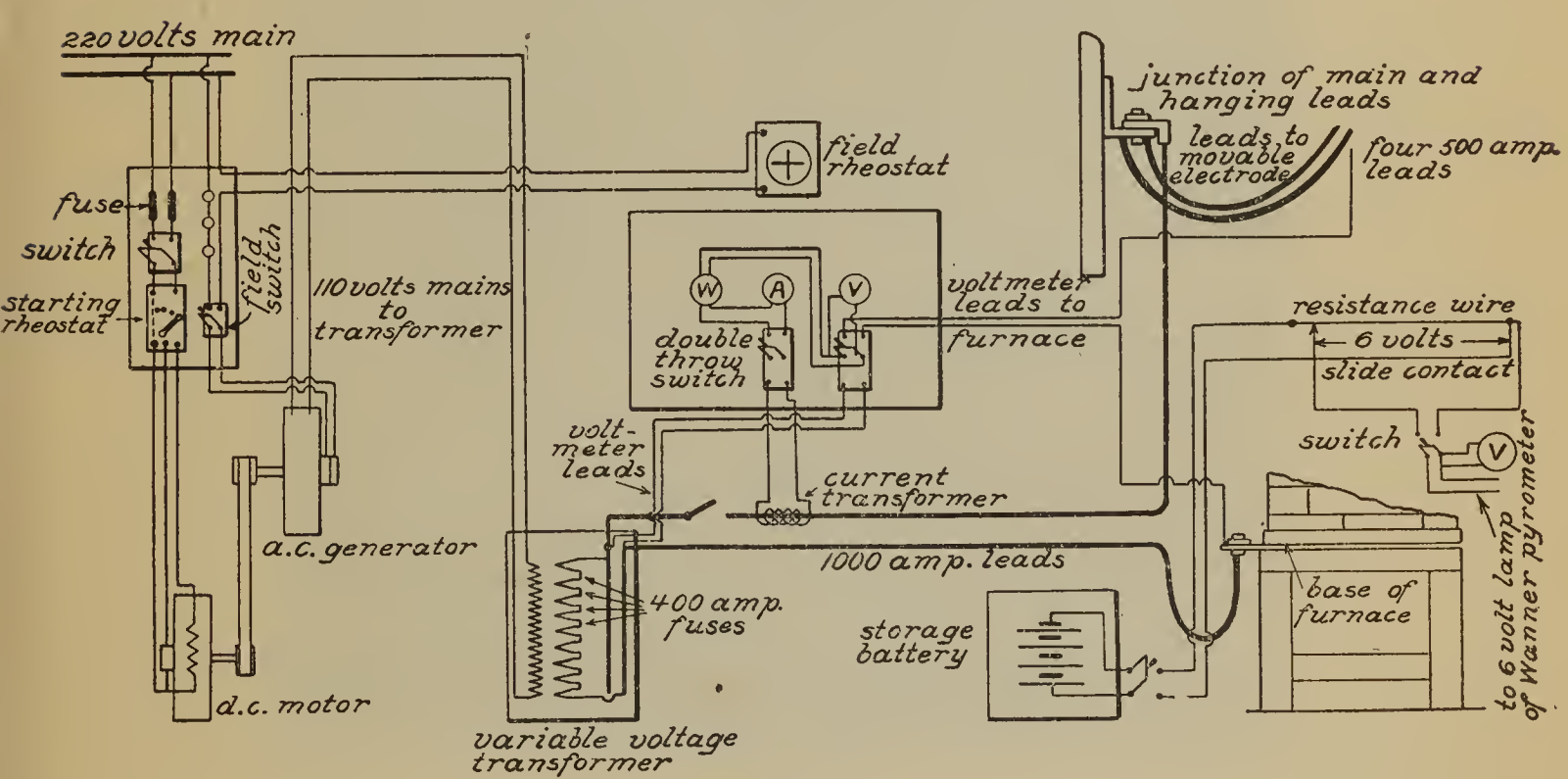


FIG. 2.

In our second run, a thin carbon plug was put in the lower end of the tube just mentioned, so as to prevent the charge running up into the tube. This plug, however, did not attain the same temperature as the charge.

For Run No. 3 a carbon tube, closed at one end as before, was placed horizontally through the furnace walls. This closed end formed a part of the base of the crucible itself. With this arangement, the molten metal was in direct contact with the surface upon which the pyrometer was focused.

As a check on observations made by this method, another tube was so arranged, with respect to the slag hole, that when the

plug was removed it would give a view of the outflowing slag just as it left the interior, and before it reached the open air.

Readings by these two methods checked, but at times the thin plug became covered on the inside with a solid film, which had to be removed by poking. Later, owing to lack of time, it became necessary to abandon the work on the gases, and the method of measuring the temperature was much simplified. Having the top of the furnace open, it was only necessary to

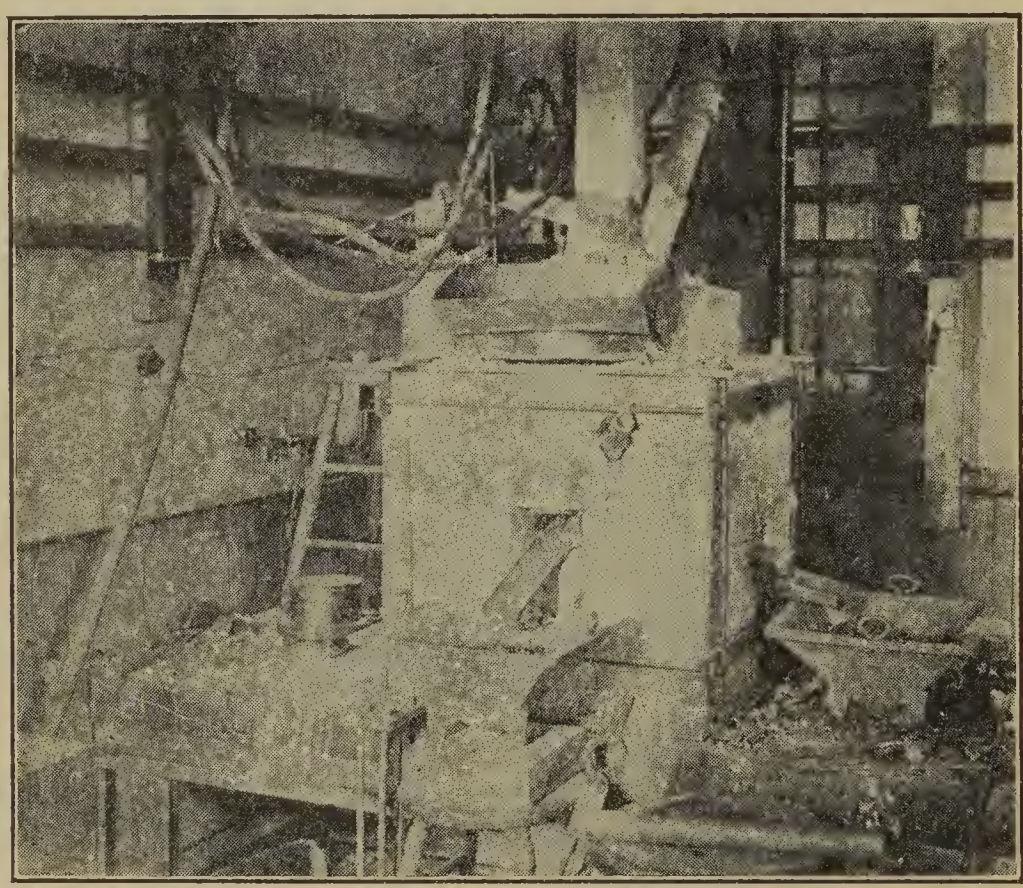


FIG. 3.

sight the pyrometer upon a clear area made in the surface of the molten charge.

The five methods which we tried of determining the temperature of the molten zone were, therefore:

(1) Open tube entering top of molten slag.
(2) Plugged tube entering top of molten slag.
(3) Horizontal plugged tube entering near base of crucible.
(4) Open tube giving a view of outflowing slag just leaving the interior.
(5) Using surface of charge as seen from the top of the furnace.

Of these, the third seems the most practical for an open-top

experimental furnace no larger than that which we used; the fifth method may also be used.

In the first six runs, the relation between temperature and the voltage, current and height of electrode was more easily observed than in the later runs, because of the large amount of slag present and the greater length of the runs, but these first runs did not give good working results, such as we were after.

A wattmeter was used after run No. 5, giving us the relation of power, input, and power factor. We noted the following

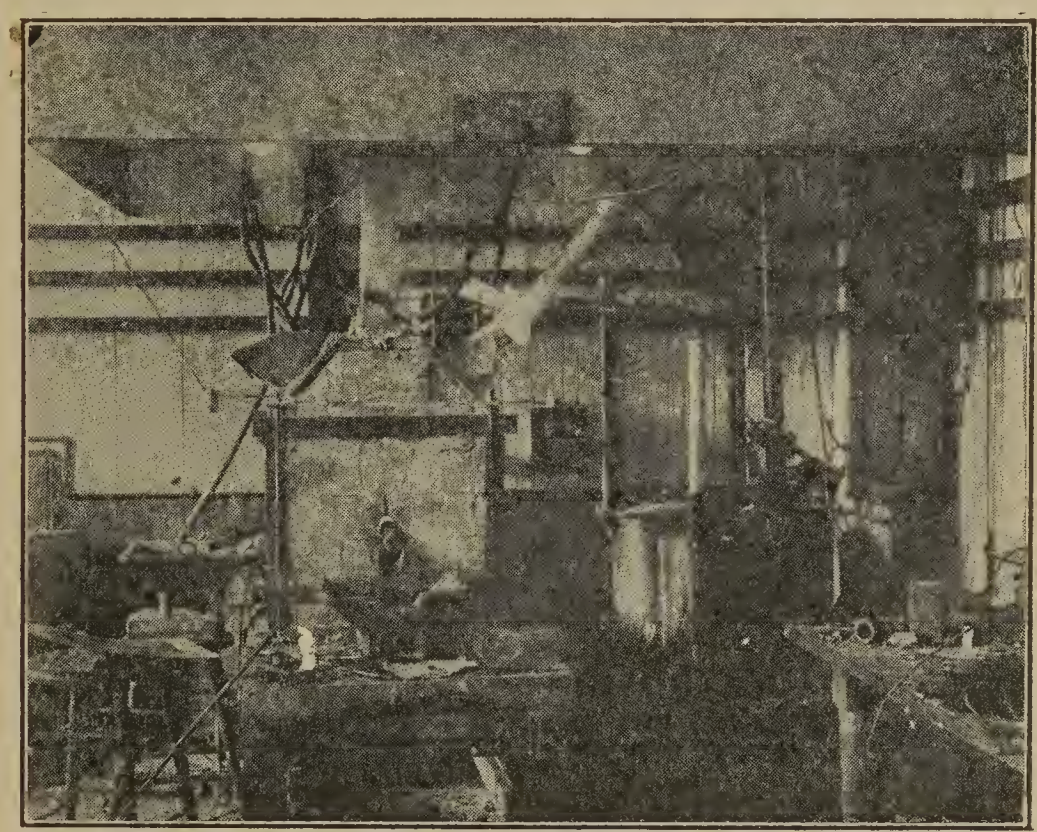


FIG. 4.

points: The current tended to increase when no addition of charge or other change in conditions was made. This is probably explained by the fact that the charge became entirely molten, and the electrical energy used in melting it served next to raise its temperature, and therefore its conductivity.

The power factor in our apparatus was approximately constant at 92 per cent. The best regulation for constant temperature was obtained, in runs 13 and 14, by maintaining the input constant.

Our experience showed that the temperature may be regulated by the energy input, by the current or voltage, and to a certain

extent by the height of the electrode, and that the temperature responds very quickly to these changes.

In runs 7 to 14 the titanium iron ore was made the basis of the tests, and a summary of No. 7 follows:

Ore treated: Titanium iron ore.
Composition of charge:

Ore	10 kgs.
Lime	2.28 kgs.
Carbon	2.25 kgs.
Length of run	55 min.
Mean volts on furnace	23.7
Mean amperes	736
Mean kilowatts	16.0
Power factor	0.94
Working temperature	1393° C.
Wt. of metal	1.32 kgs.
Wt. of slag	4.03 kgs.
H. P. yrs. per ton of pig	1.14

This run was made with a very basic slag at a comparatively low temperature, and the metal produced was analyzed for Si and Ti, and the slag for Fe.

The furnace was heated for about an hour before charging The size of the carbon was increased from what had been used in previous runs to about ¼ inch, owing to the large loss of fine dust by burning in the upper part of the furnace. The measurements of temperature in the furnace and of the outflowing slag checked fairly well. The slag was quite fluid, and the furnace emptied easily.

RUN No. 10.

Composition of charge: Same as No. 7.

Length of run	53 min.
Mean volts on furnace	28.4
Mean amperes	763
Mean kilowatts	20.8
Power factor	0.928
Working temperature	1593° C.
Wt. of metal	1.13 kgs.
Wt. of slag	1.60 kgs.
H. P. yrs. per ton of pig	2.25

In this run, as was intended, the same charge as used in Run No. 7 was smelted at a higher temperature, and, as before, analyses of the products for Si, Ti and Fe were made. We

decided next to change the composition of the charge, making it more basic. This was done in run No. 11.

RUN No. 11.

Composition of charge:	
Ore	10 kgs.
Lime	3.5 kgs.
Coke	2.25 kgs.
Length of run	31 min.
Mean volts on furnace	24
Mean amperes	1,038
Mean kilowatts	22.7
Power factor	0.910
Wt. of metal	1.60
Wt. of slag	0.90
H. P. yrs. per ton of pig	0.97

The slag obtained in this run was quite infusible and would not flow. This was probably due to the high lime content of the charge. The samples of metal obtained in these three runs were very hard and brittle. They did not have any blow holes, but contained graphite.

No analyses for carbon were made, and it was impossible to investigate the effect of temperature on the carbon content because of lack of time.

RUN No. 12.

Composition of charge: Same as No. 11.	
Length of run	29 min.
Mean volts on furnace	31.1
Mean amperes	822
Mean kilowatts	23.8
Power factor	0.928
Working temperature	1655° C.
Wt. of metal	1.77
Wt. of slag	2.27
H. P. yrs. per ton of pig	0.93

We obtained a metal finer-grained than previously and more malleable. The slag was more fluid than in Run 11. We next planned to smelt a charge low in lime at the highest possible temperature attainable with the power at our disposal.

RUN No. 13.

Composition of charge:	
Ore	4 kgs.
Lime	0.3 kgs.
Carbon	0.94

Length of run	24 min.
Mean volts on furnace	24.0
Mean amperes	1,005
Mean kilowatts	23.2
Working temperature	1922° C.
Wt. of metal	1.09 kgs.
Wt. of slag	1.71 kgs.
H. P. yrs. per ton of pig	1.22

RUN No. 14.

Composition of charge: Same as Run No. 13.

Length of run	12 min.
Mean volts on furnace	21.5
Mean amperes	811
Mean kilowatts	16.15
Power factor	0.922
Working temperature	1469° C.
Wt. of metal	.605 kg.
Wt. of slag	1.37 kg.
H. P. yrs. per ton of pig	0.79

In the last two runs the best regulation of temperature was obtained, and we used flour, carbon and molasses as a crucible lining. The slags in these two runs were both very fluid, and the charge at the lower temperature did not seem to be more difficult to fuse or less fluid than the same charge at a higher temperature. There was a difference in the appearance of the metal reduced at the two temperatures—that at the high having a fine fracture, with blow holes, while that at the lower temperature was crystalline and contained a good deal of graphite.

In determining the effect of temperature on the quality of the reduced metal, it would have been desirable to make runs on charges of different composition at one given low temperature, and at another higher than the first, but the ability to regulate the temperature was not attained soon enough to make two consecutive runs on different charges at approximately the same temperature.

The following table shows the lime ratios, per cent. of Si and Ti in the metal, per cent. of Fe in the slag, temperature of run, quality of slag, and horse-power years.

Run No.	RATIO. $\frac{CaO}{Al_2O_3 + SiO_2 + TiO_2}$	Per Cent. Si in Metal.	Per Cent. Ti in Metal.	Per Cent. Fe in Slag.	Temp. of Charge °C.	Quality of Slag.	El. H. P. Yrs. Per Ton of Pig.
7	$\frac{2.25}{2.90}$	0.05	0.00	2.95	1375	Medium fluid.	1.14
10	"	0.05	0.00	7.10	1593	Fluid.	2.25
11	$\frac{3.50}{2.90}$	0.06	0.00	6.37	1549	Infusible and viscous.	0.97
12	"	0.11	0.00	7.56	1675	"	0.93
13	$\frac{.75}{2.90}$	0.14	0.20	.....	1922	Very fluid.	1.22
14	"	0.21	0.04	.....	1469	"	0.79

We did not obtain sufficient data to draw any general conclusions in regard to the reduction of SiO_2 into the metal. The analyses show that for a given charge the amount of iron slagged off increases with the temperature.

The conditions under which the reduction of titanium into the metal begins were specially interesting. We made the large variation in lime content of the charges with the intention of determining these conditions. The analyses of the metal show that no titanium was reduced until the lime content of the slag was made small. In Run No. 13 the ratio of CaO, in the charge, to the $SiO_2 + TiO_2$ was $\frac{0.75}{2.90}$, and at the high temperature of this run the amount of Ti found in the metal was .20 per cent. At the lower temperature of Run 14, only .04 per cent. of Ti was present in the metal. In none of the previous runs, in which a higher per cent. of lime was used in the charge, was titanium reduced at all. The tests have therefore shown the character of the charge and the temperature limits necessary, that no reduction of titanium take place.

The observations on the electrical input were not taken to demonstrate the efficiency of the furnace, but rather to show the relation between power input and temperature. The results, in

point of efficiency, were, however, quite good when the small size and relatively large radiating surface of this furnace are taken into account. The lowest amount of energy required per ton of metal reduced was 0.79 horse-power years. The results of Run No. 13 show that in order to smelt a charge at 1922° C. the amount of electrical energy required above that needed to smelt the same charge at a temperature 453° lower was .18 horse-power year. This is probably quite accurate, as the run at the lower temperature was made directly after that at the high temperature, so that radiation should have been practically constant.

As this investigation was carried on during the last term of our college work, we were limited in time. We had many experimental difficulties to overcome, and were not able to make satisfactory runs till very near the end of the year. Consequently, we were not able to extend the data as far as we wished, in order to draw more accurate conclusions.

Electrochemical Laboratory,
Massachusetts Institute of Technology.

DISCUSSION.

Dr. W. R. Whitney: I believe that this kind of work is going to help us a lot here in America in just this very line, in iron and steel. I don't think we can expect the Canadian Government, or rather the Canadian Commission, to give us all the information we want along such lines as these. I think the institutions of learning like the Massachusetts Institute of Technology will do this work. Therefore, I was particularly pleased to see this published. These young men have given you a great deal of data, accurately determined. They have told you of the difficulties; of the things they would like to have done but could not do, because of lack of time and of mechanical difficulties. These points help any one who is trying to carry out such a line of complicated work. It is to be differentiated from a class of work our United States Government allowed to be done in Portland, Oregon, a year or two ago, in which a very simple experiment brought about a very

great mass of conclusions—perhaps some unwarranted conclusions.

These young men have given you a table of data, with certain figures, which show you exactly what they have done, and have not said, "There the blast furnace can be put out of business."

Mr. J. T. Morehead: I will state that I do not know the temperature in the furnace that we used, but we could make a product containing any percentage of titanium up to 83 per cent. We used an ore 37 per cent. titanic acid, 39 per cent. oxide of iron, and we got from this in the electric furnace (where we had something like 4000°) a ferro-titanium containing 35 per cent. titanium. By resmelting this we got a ferro-titanium containing anywhere from 45 to 65 per cent Ti. Using a high grade of titanium ore (a rutile) we got what Professor Moissan called a cast titanium. It turned out to be not titanium containing carbon, but a nitride carrying 79 to 81 per cent., titanium, 3 to 4 per cent. carbon and 16 to 18 per cent. nitrogen. We found that the temperature affected directly the percentage of titanium in the product.

Dr. Chamblis: What nitride of titanium did you obtain?

Mr. Morehead: We had 18 per cent. of nitrogen, 3 per cent. carbon and 79 per cent. titanium.

Mr. F. S. MacGregor: In the last two runs, our carbon was low—much lower than we used in the other runs, and that would show, if 4000° were the temperature, why so much titanium was reduced into the metal; raising the temperature tended to increase the percentage, as we found at two points.

Prof. Jos. W. Richards: I think in ten years we will look back at our discussions of these matters in a very interested way. We are in the infancy of a large industry and what we don't know about this probably amounts to over ninety-nine per cent. of what we will know inside of ten years. These experiments have given us a few points; one of them, which has been discussed. is the reduction of the titanium. We don't know the heat of the formation of the titanium oxide. It has not been determined by experiment. From the experiments of Mr. Hall, we know that in his tests iron oxide can be reduced entirely; silicon reduced entirely; titanium almost entirely; therefore there are experiments to show that titanic acid certainly is a little more difficult to reduce than silicon, and more easily reducible than aluminium.

That point, I think is fixed from Mr. Hall's work. These experiments show that iron oxide is completely reducible, practically without the reduction of any TiO_2 to the metallic state. It proves again that the reducibility of TiO_2 is above that of silicon, which gives the possibility at once of reducing in the electric furnace the titanic iron ores, with the proper temperature, to pure pig-iron with probably less titanium in it than silicon.

I think the choice of a graphite electrode was probably unwise, because of the great heat conductivity of the graphite. In electric furnace work or any kind of electrolytic furnace work the use of the graphitized electrode cools off and draws heat away from the focus of the furnace where it is most needed, and makes the temperature conditions of the furnace more difficult to obtain. I think an electrode with the lowest heat conductivity is advisable for getting a high efficiency in any electric furnace.

The idea of closing the top of the furnace air tight was a very good idea, and necessary in order to get an analysis of the gases. I think I am right in saying that probably one-half of the correct working of an electric furnace reducing iron ore, in the future, will be gauged or graded by the analyses of the gases which come off. We have not commenced to do it. The Canadian Commission did not make a gas analysis in all their work. The most important analysis around a blast furnace is the analysis of the gas. It is more important than the analysis of the ore, or slag, or pig-iron, to know what the furnace is doing; and it is unfortunate we do not have the analyses of the gases in this case. I do not know of any electric furnace reducing iron ore in which the analyses of the gases are given. I am convinced that they have been too unspeakably bad, however, to be published. An item I should like to see put in this paper would be a calculation of the proportion of fixed carbon which was used in the charge; that is one of the most ticklish things in the reduction of iron ores in the electric furnace—not the proportion of the total carbon, but the proportion of the *fixed* carbon which is useful for reduction in the lower part of the furnace.

The experiments were made on such a small scale that I do not think these power factors which were obtained have any relative significance. It could have not have been expected from such a small furnace. In a furnace of that scale the conduction loss

through the electrodes is so great that practically these power calculations, I think, have no value at all. I do not think it possible that the higher the temperature the more iron will be slagged, in practical work. I think that is a conclusion that happened to take place in the small furnace, but it is contrary to all experience in the reduction of iron ores, and it will be contrary, I am sure, to experience in reducing iron ores on a large scale in the electric furnace.

Mr. Morehead: Possibly it would be of interest to know that if, in the ferro-titanium given to the steel makers, the titanium was above 20 per cent., they would not be able to melt it and get it into their steel product, but a ferro-titanium as high as 20 per cent. could be gotten into the product to a limited extent, but with great difficulty. It works very well with 4 per cent. titanium. Car-wheel makers found great advantage and little difficulty in using 4 per cent. titanium in making car wheels, but with a higher percentage they were unable to get it into the product. We placed 65 per cent. ferro-titanium into a crucible with steel and heated it until the crucible burned away and the steel melted and ran out of the crucible, while the ferro-titanium was practically unaffected except to the extent of making the edges of the different lumps adhere.

Mr. A. E. Greene: The fact that iron increased in the slag instead of decreased as the temperature was raised, is perhaps due to the short length of the run, and the stopping of the run before complete reduction had taken place, as the carbon was pretty low.

A paper read at the Twelfth General Meeting of the American Electrochemical Society in New York City, October 18, 1907; President C. F. Burgess in the chair.

DISCUSSION OF THE EXPERIMENTS MADE AT SAULT STE. MARIE ON THE ELECTRICAL REDUCTION OF IRON ORES.

By Joseph W. Richards.

These experiments were made in 1906, and are exhaustively described in the "Report on the Experiments Made at Sault Ste. Marie, Ont., under Government Auspices, in the Smelting of Canadian Iron Ores by the Electrothermic Process," by Eugene Haanel, Ph.D., director of mines. The report was printed in Ottawa, Canada, in 1907.

The experiments were in charge of Dr. Haanel, with Dr. P. L. T. Héroult as metallurgist, and with Mr. Erik Mystrom and other members of the staff of the Mines Branch as assistants, in various capacities.

The furnace used was a simple short shaft furnace, lined with various refractory materials, such as bottom of carbon, to act as one electrode, and sides partly of carbon and silica brick or magnesite brick. The upper prismatic electrode was carbon. Minor changes in the internal profile were made during the runs, the final improved form consisting of a shaft slightly tapering outwardly downwards, and then suddenly contracting inwards, like the classical outline of an old-fashioned blast furnace.

The electrical energy obtainable was a 225 kilowatt transformer, supplied with alternating current at 2,200 volts, and furnishing current to the furnace at 50 volts. The power factor of the furnace was 0.919, *i. e.*, the apparent watts (volt-amperes) read off were multiplied by 0.919, to get the true watts on the furnace.

The analyses of the ORES TREATED is as follows:

	Negaunee Hematite.	Wilbur Mine Magnetite.	Blairton Mine Magnetite.	Calbogie Magnetite.			Roasted Pyrrhotite.	Titanic Iron Ore.
				1	2	3		
Fe	62.23	56.69	55.85	59.38	59.85	58.29	45.80	43.59
Fe^2O^3 . . .	88.90	55.42	60.74	56.24	58.00	55.31	65.43	30.30
FeO	. . . .	23.04	17.18	25.76	24.78	25 20	. . .	28.78
SiO^2 . . .	5.42	6.20	6.60	3.80	6.06	4.00	10.96	7.12
Al^2O^3 . . .	2.51	2.56	1.48	3.73	1.00	2.24	3 31	7.00
CaO	0.61	2.00	2.84	2.00	0.40	2.40	3.92	1.00
MgO . . .	0.30	6.84	5 50	3.42	6.00	4.00	3.53	4.14
MnO . . .	0.20	0.26	0.13	0.27	. . . .	. . .	Cu 0.41	TiO^2 17.82
P	0.044	0.01	0.016	0.371	0.020	0.415	0.016	0.028
S.	0.002	0.05	0.57	0.20	0.17	0.45	1.56	0.04
Loss on Ignition	2.48	3.61	4.92	3.73	3.54	5.45	Ni 2.23	Cr^2O^3 2.50

The analyses of the REDUCING AGENTS is as follows:

	Briquettes of Clay and Coke Dust.	Coke.	Coal Briquettes.	Charcoal.	Charcoal.	Electrode.
Fixed Carbon . .	69.73	90.37	55.36	74.40	55.90	95.78
Volatile Matter .	4.05	1.73	4.54	20.60	27.56	2.02
SiO^2	15.26		23.24			
Fe^2O^3 . . . . . / Al^2O^3	8.92	7.90	14.06	2.80	2.54	2.20
CaO	0.90		1.75			
MgO	0.30		0.50			
S	0.84	0.67	1.05	. . . . .	0.058	1.19
N^2O	. . . . .	. . . . .	0.20	2 20	14 00	. . . . .
P	. . . . .	. . . . .	0.015	. . . . .	. . . . .	. . . . .

ANALYSES OF FLUX USED.

	Limestone.	Fluorspar.
CaO	51.96	Not analyzed. Used only in Run No. 19.
MgO	2.09	
SiO^2	1.71	
Al^2O^3 . . . / Fe^2O^3 . . .	0.81	
P	0.004	
S	0.052	
CO^2	43.20	

Materials Used in Experiments.

Experiment.	Ore.	Reducing Agent.	Flux.
1, 2	Hematite	Coke dust and clay briquettes.	Limestone.
3, 4	"	Coke.	"
5, 6, 7, 8, 9	"	Coke dust and clay briquettes.	"
10	Magnetite	Coke dust and clay briquettes. Coke fines	Limestone, Sand.
11	Magnetite Hematite	Coke.	Sand.
12, 13	Magnetite	Charcoal.	Limestone, Sand.
14	"	"	Limestone, Sand.
15	"	Charcoal and Charcoal fines.	Limestone, Sand.
16, 17	"	Charcoal.	Limestone, Quartz.
18	Roasted Pyrrhotite	"	Limestone.
19	Titanic Iron Ore	"	Limestone, Fluorspar.

Analyses of Slags and Pig Irons Simultaneously Produced.

Slags

	Run No. 8.		Run No. 10.	Run No. 13.	Run No. 14.	Run No. 15.	Run No. 16.	Run No. 17.
	1	2						
SiO^2	29.28	34.12	35.00	39 30	36.16	24.88	30.88	33.06
Al^2O^3	15.24	15.00	28.29	18.87	18.21	22.09	9 67	15.22
CaO	35.17	45.32	20.00	15.55	23.14	38.39	36.14	33.00
MgO	2.08	2.20	10.72	27.06	20.44	10.86	20.82	16 92
FeO	16.88	2.34	2.97	1.21	0.42	0.82	0.73	0.37
(Fe)	(13.13)	(1.82)	(2.31)	(0.94)	(0 33)	(0.64)	(0.57	(0 29)
MnO	0.22	. . .	. . . .	0.35	0.05	0.04	0.14	0.32
P^2O^5	0.281	0.02	. . .	. . .	0.018	0.072	0 014	0.016
S	0.39	0.76	0.80	0.32	2.00	1.69	1.23	1.17

Pig Irons

Si	0.34	0 90	2.91	1.75	3.88	0 95	1.71	1.64
S	0.122	0 022	0.043	0.029	0.089	0.056	0.007	0.024
P	0 024	0.067	. . .	0.022	0.032	0.470	0.073	0.443
Mn	0.01	0.12	.	0.23	0.12	0.16	0.10	. . . .
Total C	4.10	4.64	4.18	4.58	3 84	3.68	4.60	3.63
Graphitic C	0.14	3.80	. . . .	3.60	3 01	1.32	4.15	2.49

The analyses of slag and pig metal when producing two special products were as follows:

Slags

	Producing Ferro-Nickel Pig.	Producing Titaniferous Pig.
SiO^2	22.84	19.34
Al^2O^3	12.07	12.64
CaO	49.60	23 90
MgO	9.27	9 28
FeO	0.26	0.72
(Fe)	(0 20)	(0 56)
MnO	0 10	0.27
CuO	0 02	. . . . .
NiO	0.02	. . . . .
TiO^2	. . . . .	17.34
Cr^2O^3	. . . . .	trace
P^2O^5	0.002	0 002
S	4.30	0.60
F	. . . . .	8.28

Pig Irons

	Producing Ferro-Nickel Pig.	Producing Titaniferous Pig.
Si	4 91	5.89
S	0.007	0.011
P	0.043	0.144
Mn	0 10	0.12
Cu	0.71	. . . . .
Ni	3.35	. . . . .
Ti	. . . . .	0.43
Cr	. . . . .	0.34
Total C	3.19	2.95
Graphitic C	2.68	2.72

Summary of the Results of the Experiments.

1.

Too much fines in charge. Material and slag occasionally thrown out. Charge sticky, preventing electrode from descending. 211 E. H. P. produced 4,484 pounds of pig iron and 3,886 pounds of slag in 34 hours, 40 minutes. Power consumption, 0.354 horse-power year per ton of pig iron.

2.

Charge too sticky to descend properly; gases escaping irregularly. Furnace worked cold. 195 E. H. P. produced 1,625 pounds of pig iron and 1,008 pounds of slag in 12 hours, 35 minutes. Power consumption, 0.328 horse-power year per ton of pig iron.

3.

Used coke as reducing agent, instead of briquettes. Gases escaped better from the more porous charge. Charge too conducting, preventing concentration of heat below the electrode, and reducing the voltage until the furnace had to be shut down, in 1 hour, 40 minutes.

4.

Furnace lining modified, so as to make the current concentrate more below the electrode. The proportion of coke in the charge was also reduced, but at 55 coke to 200 ore was still too large, and resistance fell so far that furnace had to be shut down in 2 hours, 30 minutes. Much excess of unused carbon had accumulated in the crucible, showing that more was being used than the charge could consume.

5.

Same charges as in No. 1. Charge too conducting, also contained too much carbon; electrode had to be raised, until furnace was shut down, in 7 hours, 45 minutes.

6.

Shape of interior of furnace made more cylindrical, to facilitate descent of charges. Charges unchanged. Charge too conducting, necessitating raising the electrode to keep up the voltage. Putting in a charge of pure ore helped matters, showing that the furnace was suffering from excess of carbon in the charges. The run was stopped at 6 hours, 40 minutes, in order to start afresh with charges containing less carbon.

7.

Furnace and materials unchanged, except briquettes reduced from 70 pounds to 55 pounds per 200 pounds of ore. This amount was gradually increased during the run to 65 pounds, with which gray iron was finally obtained. With 55 to 65 pounds of briquettes, the charge was not too conducting, and worked very well towards the end. 218 E. H. P. produced 4,006 pounds of pig iron and 2,525 pounds of slag in 23 hours, 40 minutes. Power consumption, 0.294 horse-power year per ton of pig iron.

8.

Height of furnace increased 12 inches; shape, a double cone.

Charge, same as in No. 7. With briquettes 60 pounds, the iron was white, from low silicon, and slag black, from high FeO. With briquettes 65 pounds, gray iron was obtained, but the resistance of the charge was at times too low, or unused carbon accumulated in the furnace, which was remedied by an occasional charge of pure ore. These facts show that carbon must be very closely regulated; too little makes low silicon, high sulphur pig iron, too much accumulates in the furnace, reducing the resistance of the charge and necessitating raising the electrode until the condition is remedied, first by a charge of ore alone, to remove the excess of accumulated carbon, second, by a change in the proportion of carbon in the regular charges, to effect a permanent cure. Working cold, the slag was high in FeO, MnO and P^2O^5, low in sulphur; working hot, the reverse occurred.

9.

Run No. 8 repeated, but with a 1-inch pipe arranged to blow in air 12 inches below the top of the charge, in order to burn the CO before it escaped, and thus to preheat the charges. The heat made the charges so sticky that they would not descend; the air blast also cut into the electrode. The attempt had to be abandoned.

The whole principle of this attempt was wrong. The air blast will consume the carbon of the charges in preference to the CO rising through them, simply producing more CO and CO^2, and wasting the solid C in the charges.

10.

Furnace same as in No. 8, but charges magnetite, in place of the hematite heretofore used; briquettes and coke fines as reducing agents. With 80 pounds of briquettes to 200 of ore, the iron was white and high in sulphur; with 5 pounds of coke fines additional, a good quality gray iron was made. With 27.18 per cent. of SiO^2, 28.60 of Al^2O^3, 28.76 of CaO, and 13.91 of MgO, the slag was too viscous; on adding sand and reducing the limestone, so that SiO^2 was 35 per cent. in the slag and CaO 20 per cent., the charge worked well. 228 E. H. P. produced 3,195 pounds of pig iron in 17 hours, 50 minutes, consuming 0.29 horse-power year per ton of pig iron.

11.

Run No. 10 was repeated, using only coke in the charge. The charge was too conducting, and as the voltage could not be reduced below 35, the difficulty was insuperable. The furnace ran only 3 hours, 20 minutes, and was then shut down, and the use of coke alone in the charge abandoned.

12.

Charcoal was used as the reducing agent, with which the furnace operated steadily at 35 to 40 volts. To 400 pounds of Wilbur magnetite, 104 pounds of charcoal was used and 28 pounds of sand as flux. The run was stopped by the iron breaking out at the tap hole. The furnace otherwise worked well. 238 E. H. P. produced, in 5 hours, 55 minutes, 1,318 pounds of pig iron, consuming only 0.243 horse-power year per ton of pig iron.

13.

The furnace was made 3 inches higher, the tap hole was made up with carbon paste, the lining was common fire-bricks. The charges were similar to those in run No. 12. The furnace had not been properly preheated before starting, and worked cold. It was thought that there was not enough carbon in the charge, and on increasing it to 120 pounds (from 104), a white iron and fluid slag was obtained. It was observed that 120 to 125 pounds of charcoal were necessary to 400 pounds of ore and 20 pounds of sand flux, to get good working. A little of this charcoal was consumed by air on top of the charge. 220 E. H. P. produced, in 61 hours, 25 minutes, 12,858 pounds of pig iron, using 21,150 pounds of ore, 6,555 of charcoal, and 1,191 of sand. The best results were obtained with 400 of ore, 125 charcoal, 27 sand. Power consumption over the whole run, 0.239 horse-power years per ton of pig iron. It was probably higher than this the first part of this run, and lower towards the end. The run was stopped to make repairs to the electric generator. Charcoal used, 1,020 pounds per ton of pig iron.

14.

Run No. 13 was repeated, using "Blairton" magnetite, charcoal, limestone and sand. The high MgO (30 per cent. at starting) made the slag very infusible. Limestone and sand

were added, so as to dilute the MgO down to 20 per cent. Gray iron was obtained with 120 pounds of charcoal to 400 of ore, using 25 of limestone and 6 of sand. The difficult fusibility of the slag and its larger amount caused a smaller output of pig iron and a higher power of consumption. 220 E. H. P. produced 11,865 pounds of pig iron in 64 hours, 30 minutes, consuming 0.273 horse-power years per ton of pig iron. Charcoal used, 1,036 pounds per ton of pig iron.

15.

Run No. 13 was repeated, using "Calabogie" magnetite, low in MgO, with charcoal and charcoal fines as the reducing agents, and limestone and sand as fluxes. The run was irregular, producing white iron at starting, with 125 pounds of charcoal to 400 pounds of ore, and gray iron with 135 pounds. The data are too irregular to justify further analysis.

16.

Run No. 13 repeated, using another variety of "Calabogie" magnetite. 145 pounds of charcoal to 400 pounds of this ore was too much; on reducing this to 125 pounds, the furnace worked much better, the output increased, and the slag was fluid. The run was stopped because of the power giving out. 224 E. H. P. produced, in 38 hours, 40 minutes, 7,150 pounds of pig iron, using 993 pounds of charcoal and consuming 0.273 horse-power year per ton of pig iron.

17.

The run No. 13 was repeated with still another variety of "Calabogie" magnetite. The furnace worked regularly with 125 pounds of charcoal to 400 of ore; the slag was very low in FeO, and the pig obtained was gray. Low-sulphur pig iron was made with CaO only 33 per cent. in the slag; practically all the phosphorus in the charge went into the pig iron. 226 E. H. P. produced 8,303 pounds of pig iron in 43 hours, 5 minutes, consuming 1,017 pounds of charcoal and 0.268 horse-power year per ton of pig iron. By mistake, an excess of carbon was put into some charges, when the resistance decreased, and the electrode had to be lifted; this was remedied by putting crude ore and quartz alone in until the accumulated carbon had been removed; then the furnace was put on the normal charge.

18.

This run was to test the production of nickel-iron alloy, low in sulphur, from roasted pyrrhotite ore carrying 2.23 per cent. of nickel, 45.80 of iron, and 1.56 of sulphur. By making a charge of 400 ore, 105 charcoal, and 40 limestone, the sulphur was kept at the surprisingly low figure of 0.006 in the metal, and the nickel down to 0.015 in the slag. 222 E. H. P. produced 7,336 pounds of alloy, in 56 hours, 20 minutes, consuming 1,104 pounds of charcoal and 0.39 horse-power year per ton of alloy.

19.

This was a hurried qualitative experiment, to test the production of pig iron from titanic iron ore. The ore was mixed with charcoal, limestone and fluorspar, making a fluid slag with 17 to 18 per cent. of TiO^2, and a pig iron with only 0.43 per cent. Ti. The test was cut short by the bad condition of the furnace, but proved conclusively the possibility of thus producing good pig iron.

Run No. 1. Balance Sheet.

Per 1,000 of Pig Iron Produced.

Hematite (1,740 lbs.)		Pig Iron. Assumed from Run 8.		Slag.		Gases.	
Fe^2O^3	1,547	Fe	943	FeO	180	O	424
SiO^2	94	Si	9	SiO^2	85	O	10
Al^2O^3	44			Al^2O^3	44		
CaO	11			CaO	11		
MgO	5			MgO	5		
MnO	3	Mn	1	MnO	2		
P	0.77	P	0.67	P^2O^5	0.23	O	0.13
S	0 03	S	0.03				
H^2O	43					H^2O	43
Briquettes (609 lbs.)							
Fixed C	425	C	46			C	379
Vol. Mtr.	25					Vol. Mtr.	25
SiO^2	93			SiO^2	93		
Fe^2O^3 / Al^2O^3	54			Fe^2O^3 / Al^2O^3	54		
CaO	5			CaO	5		
MgO	2			MgO	2		
S	5	S	0.19	S	4.81		
Limestone (812 lbs.)							
				Ca	6.5		
CaO	422			CaO	413	O	2.6
MgO	17			MgO	17		
SiO^2	14			SiO^2	14		
Al^2O^3 / Fe^2O^3	7			Al^2O^3 / Fe^2O^3	7		
P	0.03			P^2O^5	0.07	O	0.04
S	0.42			S	0.42	CO^2 351	C 96 / O 255
CO^2	351						
	3,161		1,000		944		1235

C in gases, 475
O " " 692
CO = 1,005 lbs.
CO^2 = 162 "
CO = 12,760 ft.^{3}
CO^2 = 1,309 "
$\frac{CO}{CO^2}$ = 9.7 (by vol.)

Run No. 8. Balance Sheet.

Per 1,000 of Pig Iron Produced.

Charges.	Pig Iron.	Slag.	Gases.
Hematite (1,667 lbs.)			
Fe^2O^3 . 1,482	Fe 943	FeO . . . 122	O 417
SiO^2 . . 90	Si 9	SiO^2 . . . 71	O 10
Al^2O^3 . . 42		Al^2O^3 . . 42	
CaO . . . 10		CaO . . 10	
MgO . . 5		MgO . . . 5	
MnO . . 3	Mn . . . 1	MnO . . . 2	
P^2O^5 . . 1.68	P 0.67	P^2O^5 . . . 0.15	O 0.2
S 0.03	S 0.03		O 0.86
H^2O . . 41			H^2O . . 41
Briquettes (507 lbs.)			
Fixed C. . 354	C 46		C 308
Vol. Mtr . 23			Vol. Mtr. 23
SiO^2 . . 77		SiO^2 . . . 77	
Al^2O^3 } Fe^2O^3 } . 45		Al^2O^3 } Fe^2O^3 } . 45	
CaO . . . 5		CaO . . . 5	
MgO . . . 2		MgO . . . 2	
S 4	S 0.19	S 3.81	
Limestone (417)			
CaO . . . 217		Ca 5.04	O 2
MgO . . . 9		CaO . . . 215	
SiO^2 . . . 7		MgO . . . 9	
Al^2O^3 } Fe^2O^3 } . 3		SiO^2 . . . 7	
P^2O^5 . . . 0.03		Al^2O^3 } Fe^2O^3 } . 3	
S 0.22		P^2O^5 . . . 0.03	
CO^2 . . . 180		S 0.22	CO^2 180 { C 49, O 131 }
2,591	1,000	624	982

C in gases, 357
O " " 561
CO = 684 lbs.
CO^2 = 234 "
CO = 8,696 ft.^{3}
CO^2 = 1,891 "

$$\frac{CO}{CO^2} = 4.6 \text{ (by vol.)}$$

		CALCULATED.			ANALYSES.	
SLAG	SiO^2	155	=	25%	34.12%	29.28
	Al^2O^3	84	=	13	15.00	15 24
	CaO	230	=	37	45.32	35.17
	MgO	16	=	2	2.20	2.08
	FeO	127	=	20		16 88

HEAT BALANCE SHEET, PER 1,000 POUNDS OF PIG IRON.

AVAILABLE.

Electric Current:	1,222 H. P. hours × 1,400 = 1,710,800 lb. cal.		= 67%
C to CO	293 × 2,430 = 712,000		
C to CO^2	15 × 8,100 = 121,500	833,500	33%
		2,544,300	

DISTRIBUTION.

Reduction of Fe^2O^3	= 943 × 1,746 =	1,646,500	
" " SiO^2	= 9 × 7,500 =	67,500	
" " MnO	= 1 × 1,653 =	1,650	
" " CaO	= 5 × 3,250 =	15,750	
" " P^2O^5	= 0.67 × 5,890 =	3,900	1,735,300 = 69%
Heat in melted pig	= 1,000 × 350		350,000 = 14
" " " slag	= 624 × 550		343,200 = 14
" " hot gases			
CO	$\frac{684}{1.26}$ × 330 = 179.190		
CO^2	$\frac{234}{1.98}$ × 590 = 139,240		
H^2O	$\frac{41}{0.81}$ × 490 = 20,700		
H^2O	41 × 606 = 24,850		363,980 = 14%
			111%

NOTES ON 8.

If ratio $\frac{CO}{CO^2}$ in gases had been 2 to 1.

O as CO	= 280.5	C = 210
O as CO^2	= 280.5	C = 105
	Sum	315
C in CO^2 of flux		= 49
C from fixed C		= 266
C for pig iron		= 46
C from fuel		= 302

Weight of briquettes required = 302 ÷ 0.6973 = 433 lbs.
Saving of " " = 507 — 433 = 74 " = 14.6%

Heat obtained from fuel in first case:

C to CO	= 293 × 2,430 = 712,190	lbs. cal.
C to CO^2	= 15 × 8,100 = 121,500	" "
	833,690	" "

Heat obtained from smaller amount of fuel in second case :

C to CO	= 210 × 2,430	= 510,300	lbs. cal.
C to CO^2	= 56 × 8,100	= 453,600	" "
		963,900	" "
Excess obtained in second case		= 130,210	" "
Saving = 130,210 ÷ 641		= 203.1	H. P. hours saved.
		= 0.032	" year.
		= 13.6%	saving in power.

Run No. 13. Balance Sheet.

Per 1,000 of Pig Iron Produced.

Charges.	Pig Iron.	Slag.	Gases.
MAGNETITE (1,645)			
Fe^2O^3 . . 912	Fe . . . 638		O 274
FeO . . . 379	Fe 295		O 84
SiO^2 . . . 102	Si 17.5	SiO^2 . . . 64	O 20
Al^2O^3 . . 41		Al^2O^3 . . 41	
CaO . . . 33		Ca 1.04	O 0.4
MgO . . . 113		CaO . . . 32	
MnO . . . 4	Mn 2.3	MgO . . . 113	
P^2O^5 . . . 0.37	P 0.22	MnO . . . 1	O 1
S 0.82	S 0.29	S 0.53	
CO^2, etc . 59			
CHARCOAL (510)			
Fixed C. . 285	C 46		C . . . 239
Vol. Mtr . 140			V. M . . 140
H^2O . . . 71			H^2O . . 72
SiO^2 . . . 13		SiO^2 . . . 13	
S 0.30		S 0.30	
SAND (93)			
SiO^2 . . . 76		SiO^2 . . . 76	
Fe^2O^3 . . .			
Al^2O^3 . 13		Al^2O^3 . . 13	
CaO . . . 1		CaO . . . 1	
MgO . . . 1		MgO . . . 1	
Alk., etc . 1		Alk. 1	
2,248	999	358	829

C in gases, 239		CALCULATED.			ANALYSIS.
O " " 380	SLAG	SiO^2 153	= 43	%	39.30
CO " " 551		Al^2O^3 54	= 15		18.87
CO^2 " " 168		CaO 33	= 9		15.55
Vol. CO = 7,000 ft.^{3}		MgO 114	= 35		27.06
" CO^2 = 1,358		S 0 83	= 0.23		0.32
$\frac{CO}{CO^2}$ = 5.2 (by vol.)					

Heat Balance Sheet, Per 1,000 Pounds of Pig Iron.

AVAILABLE.

Electric Current :	104 × 6.8 H. P. hours × 1,400 =	1,465,500 lb. cal.	= 64%
C to CO	195 × 2,430 = 473 850		
C to CO^2	46 × 8,100 = 372,600	846,450 " "	= 36%
		2,311,950 " "	

DISTRIBUTION.

Reduction of Fe^2O^3	638 × 1,746 = 1,113,950		
" " FeO	295 × 1,173 = 346.050	1,460,000	
" " SiO^2	17.5 × 7,500 =	131,250	
" " CaO	1 × 3,250 =	3,250	
		1,594,500	= 68%
Heat in melted pig iron	1,000 × 350 =	350,000	= 15
" " " slag	358 × 550 =	196,900	= 8
" " hot gases (at 1,000°):			
CO	$\frac{451}{1.26}$ × 330 = 118,140		
CO^2	$\frac{168}{1.98}$ × 590 = 50,150		
H^2O	71 × 606 = 43,039		
H^2O	$\frac{71}{0\ 81}$ × 490 = 42,920	254,240	= 11%
			102%

As in the case of run No. 8, there is more heat accounted for than was available. Part of this may have come from the heat of oxidation of CO in the upper part of the furnace, by air which found its way in. There seems to be no other possible source.

Conclusions.

1. Too much carbon was used in every case, not allowing a good utilization of the heat of oxidation of carbon in the furnace. A *smaller* proportion of carbon, more perfectly consumed to CO^2, would generate *more* heat, and thus help the furnace along.

2. In the runs given, the electric current furnished about two-thirds of the energy required for all purposes, the carbon, one-third.

3. Gas analyses, temperature of gases and calorimetric determinations of the heat in liquid pig iron and slag should be made in all cases, since important data depend on them.

4. The consumption of fixed carbon was 240 to 380 pounds per 1,000 of pig iron = 24 to 38 per cent. of the weight of pig-

iron. With a larger production of CO^2, even lower than 24 per cent. should be possible, for in this case only one-fifth of the carbon burned to CO^2.

5. The conditions for economical reduction and large output are:

(a) A high column of charge, to allow of reduction by CO gas.

(b) Uniform size of charge, and not too fine, so that the gases may evenly, slowly and uniformly permeate and reduce the charge.

(c) To be content with white pig iron. If high-silicon, gray iron is desired, add ferro silicon made in another furnace to the melted material. If sulphur is high, add carborundum waste or a silicon-calcium ferro alloy. These will make the iron gray and remove sulphur without requiring the whole charge to be very intensely heated to the high temperature otherwise required. This division of labor, employing a small furnace at a very high temperature to make ferro-silicon, and running the large reduction furnace at a moderate temperature to make pig-iron, seems to be a desirable economic combination.

A paper read in abstract by Dr. E. F. Roeber at the Twelfth General Meeting of the American Electrochemical Society, in New York City, October 18, 1907; President C. F. Burgess in the chair.

MATHEMATICS OF THE INDUCTION FURNACE.

By Gustave Gin.
(Translated by E. F. Roeber.)

The induction furnace is essentially a transformer, with a short-circuited secondary, consisting of a single turn or ring.

The abnormal features of such a transformer require a careful study of the conditions under which its efficiency becomes a maximum.

The unusual dimensions of the magnetic circuit and the impossibility of distributing the primary winding over the whole periphery are causes of considerable magnetic stray fluxes. On the other hand, the size of the secondary ring results in a large coefficient of self-induction and a corresponding reduction of the power factor in the primary. Finally, the frequency of the supply current is an important factor.

For all these reasons, it is useful to study in detail under what conditions the cost of construction will be a minimum, and the electric and thermic efficiency a maximum. Before we deal with a special example, we will discuss the more general problem of a transformer with considerable magnetic stray fluxes, and we will assume that this transformer has two symmetrically arranged cores on which the primary windings are placed, being connected in series, as shown in Figs. 3 or 8.

We will use the following notation:

e_1, E_1, the instantaneous and effective values respectively of the e. m. f. at the terminals of the primary.

i_1, I_1, i_2, I_2, the instantaneous and effective values respectively of the primary and secondary currents.

φ, Φ, the instantaneous and effective values respectively of the magnetic flux common to the secondary and the two primaries.

φ_1, Φ_1, the instantaneous and effective values respectively of the two fluxes which surround the two primaries without surrounding the secondary.

φ_2, Φ_2, the instantaneous and effective values respectively of the flux which surrounds the secondary without surrounding the primaries.

$2\mathfrak{R}$, the reluctance of one of the magnetic circuits; $\mathfrak{R}$, the reluctance of the two magnetic circuits.

$\mathfrak{R}_1$ and $\mathfrak{R}_2$, the reluctances of the circuits through which the fluxes φ_1 and φ_2 pass.

n_1, the number of turns of each of the primary circuits.

n_2, the number of turns of the secondary circuit.

If we neglect the ohmic drop in the primary, we can write the fundamental equations as follows:

$$\frac{e_1}{2} = n_1 \frac{d\left(\frac{\varphi}{2}\right)}{d\,t} + n_1 \frac{d\left(\frac{\varphi_1}{2}\right)}{d\,t}$$

$$O = r_2\, i_2 + n_2 \frac{d\,\varphi}{d\,t} + n_2 \frac{d\,\varphi_2}{d\,t}$$

$$2\,\mathfrak{R}\left(\frac{\varphi}{2}\right) = 4\,\pi\, n_1\, i_1 + 4\,\pi\, n_2\, i_2$$

$$2\,\mathfrak{R}_1\left(\frac{\varphi_1}{2}\right) = 4\,\pi\, n_1\, i_1$$

$$2\,\mathfrak{R}_2\left(\frac{\varphi_2}{2}\right) = 4\,\pi\, n_2\, i_2$$

We can simplify these equations, and write them as follows:

(1) $$e_1 = n_1 \frac{d\,\varphi}{d\,t} + n_1 \frac{d\,\varphi_1}{d\,t}$$

(2) $$O = r_2\, i_2 + n_2 \frac{d\,\varphi}{d\,t} + n_2 \frac{d\,\varphi_2}{d\,t}$$

(3) $$\mathfrak{R}\,\varphi = 4\,\pi\, n_1\, i_1 + 4\,\pi\, n_2\, i_2$$

(4) $$\mathfrak{R}_1\,\varphi_1 = 4\,\pi\, n_1\, i_1$$

(5) $$\mathfrak{R}_2\,\varphi_2 = 4\,\pi\, n_2\, i_2$$

From the equations (1), (2), (4) and (5), we get

(6) $$e_1 = n_1 \frac{d\,\varphi}{d\,t} + \frac{4\,\pi\, n_1^2}{\mathfrak{R}_1} \frac{d\,i_1}{d\,t}$$

(7) $$O = r_2\, i_2 + n_2 \frac{d\,\varphi}{d\,t} + \frac{4\,\pi\, n_2^2}{\mathfrak{R}_2} \frac{d\,i_2}{d\,t}$$

By differentiating equation (3) and by inserting the value of $\frac{d\varphi}{dt}$ in (7), and simplifying the equations somewhat, we get

$$(8) \quad O = r_2 i_2 + 4\pi n_2^2 \frac{\mathfrak{R} + \mathfrak{R}_2}{\mathfrak{R}\mathfrak{R}_2} \frac{d i_2}{d t} + \frac{4\pi n_1 n_2}{\mathfrak{R}} \frac{d i_1}{d t}$$

FIG. 1.

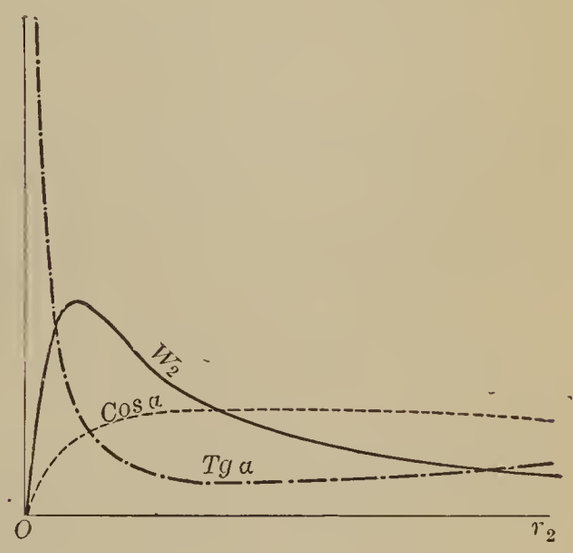


FIG. 2.

and if we calculate $\frac{d i_1}{d t}$ from (6) and (3) and insert in (8), we have

$$(9) \quad O = r_2 i_2 + \frac{4\pi n_2^2}{\mathfrak{R}_2} \frac{\mathfrak{R} + \mathfrak{R}_1 + \mathfrak{R}_2}{\mathfrak{R} + \mathfrak{R}_1} \frac{d i_2}{d t} + \frac{\mathfrak{R}_1}{\mathfrak{R} + \mathfrak{R}_1} \frac{n_2}{n_1} e_1$$

The graphical solution[1] of equation (8) gives the relation between I_1 and I_2.

The time is counted from the phase of the secondary current, I_2. We make, in Fig. 1,

$$OA = r_2 I_2$$

$$AB = 4\pi n_2^2 \frac{\mathfrak{R} + \mathfrak{R}_2}{\mathfrak{R}\,\mathfrak{R}_2} \omega I_2$$

AB being 90° in advance of OA in phase. From equation (8), it follows that the vector BO represents

$$\frac{4\pi n_1 n_2}{\mathfrak{R}} \frac{d i_1}{d t}$$

and we have

$$BO = \frac{4\pi n_1 n_2}{\mathfrak{R}} \omega I_1$$

The angle β represents the phase difference between $\frac{d i_2}{d t}$ and $\frac{d i_1}{d t}$ or between the currents i_1 and i_2.

In the right-angle triangle OAB, we have

$$\frac{4\pi n_1 n_2}{\mathfrak{R}} \omega I_1 = \sqrt{r_2^2 I_2^2 + \frac{16\pi^2 n_2^4 \omega^2}{\mathfrak{R}^2} \frac{(\mathfrak{R} + \mathfrak{R}_2)^2}{\mathfrak{R}_2^2} I_2^2}$$

hence

$$(10) \qquad \frac{n_1 I_1}{n_2 I_2} = \sqrt{\left(\frac{\mathfrak{R} + \mathfrak{R}_2}{\mathfrak{R}_2}\right)^2 + \left(\frac{\mathfrak{R}\, r_2}{4\pi n_2^2 \omega}\right)^2}$$

$$(11) \qquad \text{tang}\,\beta = -\frac{AO}{BA} = -\frac{\mathfrak{R}\,\mathfrak{R}_2\, r_2}{4\pi n_2^2 \omega (\mathfrak{R} + \mathfrak{R}_2)}$$

If $\mathfrak{R}$ is negligible in comparison with $\mathfrak{R}_2$, the equations (10) and (11) assume the form,

$$(12) \qquad \frac{n_1 I_1}{n_2 I_2} = \sqrt{1 + \left(\frac{\mathfrak{R}\, r_2}{4\pi n_2^2 \omega}\right)^2}$$

$$(13) \qquad \text{tang}\,\beta = -\frac{\mathfrak{R}\, r_2}{4\pi n_2^2 \omega}$$

[1] NOTE OF TRANSLATOR.—In what follows, Mr. Gin evidently uses the relation $i_2 = I_2 \sin(\omega t)$, where $\omega = 2\pi n$ and n the frequency and t the time, so that $\frac{di_2}{dt} = \omega I_2 \cos(\omega t)$, with regard to phase in quadrature with $OA = r_2 I_2$. It appears therefore that $I_1 I_2$ are intended to represent the maximum values, not the effective values as stated above. Of course, in the vector diagram Fig. 1, the vectors may represent just as well effective values as maximum values, since the ratio between the two is a constant.

E_2 is the total e. m. f. induced in the secondary, and in consideration of $r_2 I_2 = E_2$, by means of the graphical solution of equation (9) (Fig. 1), we get, in the same way as we calculated the ratio of I_1 to I_2 above, the following equations for the right-angle triangle OAC:

$$(14)\quad \frac{E_1}{E_2} = \frac{n_1}{n_2}\,\frac{\mathfrak{R} + \mathfrak{R}_1}{\mathfrak{R}_1}\sqrt{1 + \left[\frac{4\,\pi\, n_2{}^2\,\omega\,(\mathfrak{R} + \mathfrak{R}_1 + \mathfrak{R}_2)}{(\mathfrak{R} + \mathfrak{R}_1)\,\mathfrak{R}_2\, r_2}\right]^2}$$

$$(15)\quad \tan\delta = -\frac{4\,\pi\, n_2{}^2\,\omega\,(\mathfrak{R} + \mathfrak{R}_1 + \mathfrak{R}_2)}{(\mathfrak{R} + \mathfrak{R}_1)\,\mathfrak{R}_2\, r_2}$$

δ being the phase difference between E_1 and E_2 (or I_2).

If we neglect $\mathfrak{R}$, in comparison with $\mathfrak{R}_1$ and $\mathfrak{R}_2$, the equations (14) and (15) assume the form,

$$(16)\quad \frac{E_1}{E_2} = \frac{n_1}{n_2}\sqrt{1 + \left[\frac{4\,\pi\, n_2{}^2\,\omega\,(\mathfrak{R}_1 + \mathfrak{R}_2)}{\mathfrak{R}_1\,\mathfrak{R}_2\, r_2}\right]^2}$$

$$(17)\quad \tan\delta = -\frac{4\,\pi\, n_2{}^2\,\omega\,(\mathfrak{R}_1 + \mathfrak{R}_2)}{\mathfrak{R}_1\,\mathfrak{R}_2\, r_2}$$

The equation (14) may be written

$$(18)\quad \frac{E_1}{E_2} = \frac{n_1}{n_2}\,\frac{\mathfrak{R} + \mathfrak{R}_1}{\mathfrak{R}_1}\,\frac{1}{\cos(\pi - \delta)}$$

Phase difference of transformer.—The angle α is the phase difference between E_1 and I_1, *i. e.*, "the phase difference of the transformer." Since the sum of α and BOC is 90°, we can write[2]

$$(19)\quad \tan\alpha = \frac{\mathfrak{R}\, r_2}{4\,\pi\, n_2{}^2\,\omega}\,\frac{\mathfrak{R} + \mathfrak{R}_1}{\mathfrak{R}_1} + \frac{4\,\pi\, n_2{}^2\,\omega}{r_2}\,\frac{\mathfrak{R} + \mathfrak{R}_2}{\mathfrak{R}_2}\,\frac{\mathfrak{R} + \mathfrak{R}_1 + \mathfrak{R}_2}{\mathfrak{R}_1\,\mathfrak{R}_2}$$

or if $\mathfrak{R}$ is negligible in comparison with $\mathfrak{R}_1$ and $\mathfrak{R}_2$,

$$(20)\quad \tan\alpha = \frac{\mathfrak{R}\, r_2}{4\,\pi\, n_2{}^2\,\omega} + \frac{4\,\pi\, n_2{}^2\,\omega}{r_2}\,\frac{\mathfrak{R}_1 + \mathfrak{R}_2}{\mathfrak{R}_1\,\mathfrak{R}_2}$$

If r_2 is very small, we can write

$$(21)\quad \tan\alpha = \frac{4\,\pi\, n_2{}^2\,\omega}{r_2}\,\frac{\mathfrak{R}_1 + \mathfrak{R}_2}{\mathfrak{R}_1\,\mathfrak{R}_2}$$

[2] NOTE OF TRANSLATOR.—This result is obtained as follows: Since $\alpha = 2\pi - \beta - \delta$ we have

$$\tan\alpha = \frac{-\tan\beta - \tan\delta}{1 - \tan\beta\,\tan\delta}$$

By inserting the values from (11) and (15) we get equation (19).

Discussion of the formula of phase difference.—When the transformer is not loaded, r_2 is infinitely large, and tang α is also infinitely large, hence the phase difference between the current I_1 and the potential difference E_1 is 90°. In reality, however, α is less than 90°, since we have neglected the ohmic drop in the primary, as well as the effect of hysteresis and eddy currents.

When r_2 decreases, although remaining still very large, the first term on the right hand of equation (19) is predominant, so that tang α and α decrease with decreasing r_2. For the value,

$$(22) \quad r_2 = \frac{4\pi n_2^2 \omega}{\mathfrak{R}_2} \sqrt{\frac{(\mathfrak{R} + \mathfrak{R}_2)(\mathfrak{R} + \mathfrak{R}_1 + \mathfrak{R}_2)}{\mathfrak{R}(\mathfrak{R} + \mathfrak{R}_1)}} = r_2^1$$

the two terms on the right hand of equation (19) become equal, and we have

$$(23) \quad \text{tang}\,\alpha = \frac{2}{\mathfrak{R}_1 \mathfrak{R}_2} \sqrt{\mathfrak{R}(\mathfrak{R} + \mathfrak{R}_1)(\mathfrak{R} + \mathfrak{R}_2)(\mathfrak{R} + \mathfrak{R}_1 + \mathfrak{R}_2)}$$

This is the minimum value of tang α. When r_2 decreases still further, the second term is the predominant one, so that tang α and α now increase with decreasing r_2.

Conditions of favorable phase difference.—If the first term predominates, there should be employed

a small reluctance $\mathfrak{R}$,
a high frequency,
a large number of turns on the secondary, and
the primary stray flux should be very small, or, in other words, $\mathfrak{R}_1$ should be large compared with $\mathfrak{R}$.

On the other hand, if the second term predominates, there should be employed

a small reluctance $\mathfrak{R}_1$,
a low frequency,
a small number of turns on the secondary, and
the magnetic stray fluxes should be small, *i. e.*, $\mathfrak{R}_1$ and $\mathfrak{R}_2$ very large.

Determination of power in secondary.—Since E_2 is the total e. m. f., as defined above, the power consumed in the secondary is

$$W_2 = \frac{E_2^2}{r_2}$$

and on account of formula (14),

$$(24)\quad W_2 = \frac{\Re_1^{\,2}}{(\Re + \Re_1)^2} \; \frac{n_2^{\,2}\, E_1^{\,2}}{n_1^{\,2}\left[r_2 + \dfrac{16\,\pi^2\, n_2^{\,4}\,\omega^2 (\Re + \Re_1 + \Re_2)^2}{\Re_2^{\,2}\, r_2\, (\Re + \Re_1)^2}\right]}$$

or, according to equation (18),

$$(25)\qquad W_2 = \frac{\Re_1^{\,2}}{(\Re + \Re_1)^2}\, \frac{n_2^{\,2}}{n_1^{\,2}}\, \frac{E_1^{\,2}}{r_2} \cos^2 (\pi - \delta)$$

From Fig. 1, we see that

$$\alpha = \pi - \delta + \pi - \beta$$

or

$$\pi - \delta = \alpha - (\pi - \beta)$$

hence,[3]

$$(26)\qquad W_2 = \frac{\Re_1^{\,2}}{(\Re + \Re_1)^2}\, \frac{n_2^{\,2}\, E_1^{\,2}}{n_1^{\,2}\, r_2} \cos^2 \alpha \cos^2 (\pi - \beta)$$
$$[1 + \text{tang}\, \alpha\, \text{tang}\, (\pi - \beta)]^2$$

As a first approximation, we may write

$$(27)\qquad W_2 = \frac{n_2^{\,2}\, E_1^{\,2}}{n_1^{\,2}\, r_2} \cos^2 \alpha$$

Formula 24 shows that for

$$r_2 = 0$$
$$W_2 = 0$$

When r_2 increases, W_2 also increases up to its maximum value,

$$(28)\qquad W_2 = \frac{\Re_1^{\,2}\, \Re_2\, E_1^{\,2}}{8\, \pi\, n_1^{\,2}\, \omega\, (\Re + \Re_1)\, (\Re + \Re_1 + \Re_2)}$$

which occurs for

$$(29)\qquad r_2 = \frac{4\, \pi\, n_2^{\,2}\, \omega\, (\Re + \Re_1 + \Re_2)}{\Re_2\, (\Re + \Re_1)}$$

The corresponding phase difference is given by the formula,

$$(30)\qquad \text{tang}\, \alpha = 1 + \frac{2\, \Re\, (\Re + \Re_1 + \Re_2)}{\Re_1\, \Re_2}$$

which value is near unity, *i. e.*, $\alpha = 45^\circ$.

[3] Note of Translator:—Equation (26), as given above does not seem to simplify matters, but it is at least correct. In Mr. Gin's French manuscript, equation (26) reads as follows:

$$W_2 = \frac{\Re_1^{\,2}}{(\Re + \Re)^2}\, \frac{n_2^{\,2}\, E_1^{\,2}}{n^2\, r_2} \cos^2 \alpha\, [1 + \sin \alpha\, \text{tang}\, (\pi - \beta)]^2$$

which is evidently not correct. Equation (27) is correct if $\Re$ is negligible compared with $\Re_1$, and if the error committed in substituting α for $\pi - \delta$ is negligible.

Applications of the preceding formulas.—In Fig. 2 we have plotted the curves of the variation of W_2 and tang α as function of r_2 for a hypothetical transformer. This figure shows clearly the conclusions arrived at above.

PRACTICAL CALCULATION OF A GIN FURNACE.

1. First method: Primary windings placed on the outer vertical legs of the iron cores.

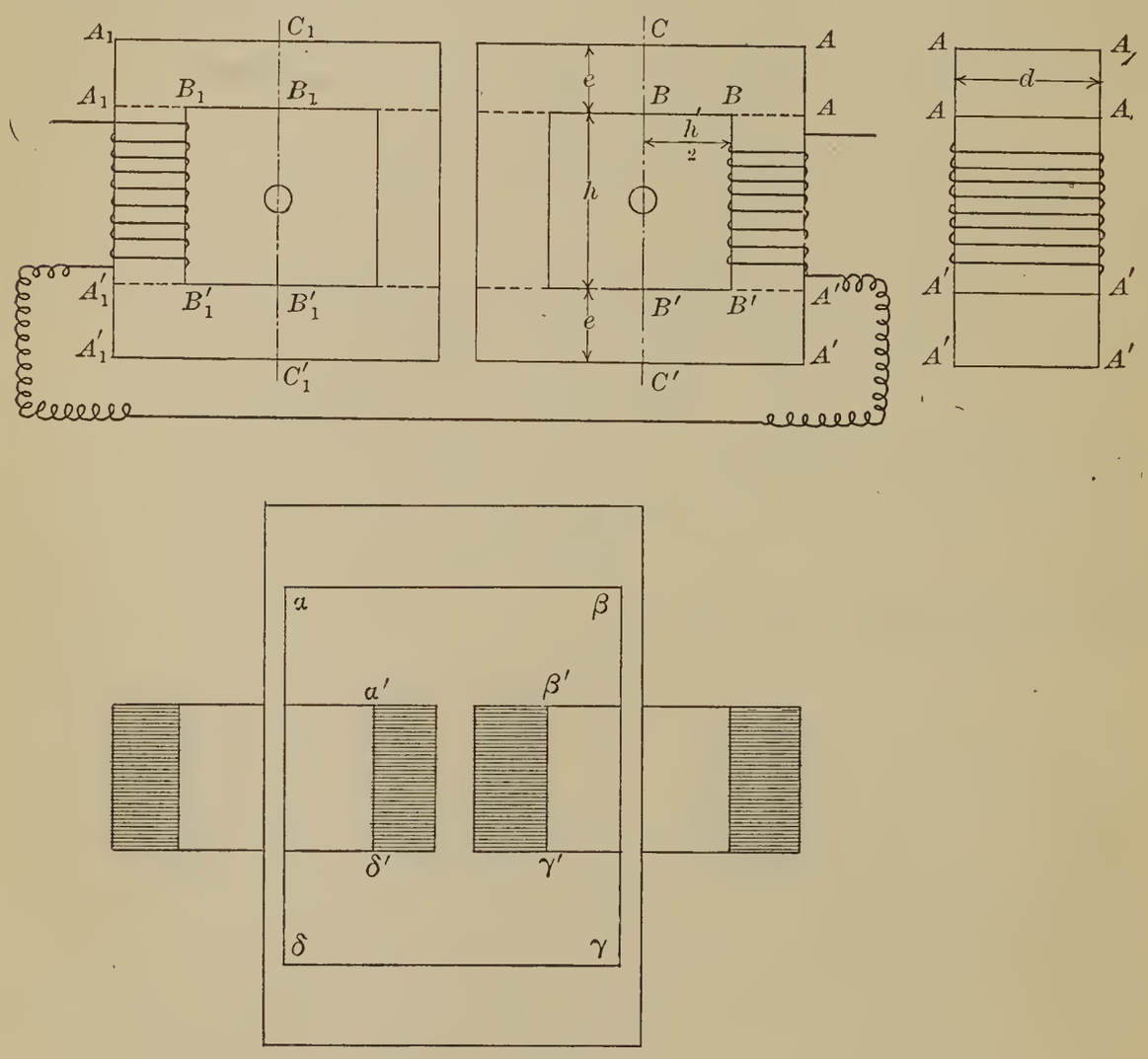


FIG. 3.

Let us consider the special transformer represented by the Gin induction furnace with circulation. The magnetic circuit has the form indicated in Fig. 3. The primary windings cover completely the vertical outer legs of the two iron cores, and the secondary is represented by a single rectangular turn. To simplify matters, we will assume it to be a cylinder in section, two opposite sides having the radius r, and the other two the radius r^1.

CALCULATION OF RELUCTANCES.

a. Calculation of $\mathfrak{R}$.—The reluctance $\mathfrak{R}$ is that of the two magnetic circuits. The reluctance of one of them is given by the formula,

$$2\,\mathfrak{R} = \frac{l}{\mu\, s}$$

where l is the mean length of the magnetic circuit and s the cross-section of the core. We therefore get

$$\mathfrak{R} = \frac{l}{2\,\mu\, s} = \frac{h + h^1 + e}{\mu\, d\, e} \tag{31}$$

b. Calculation of $\mathfrak{R}_1$.—This is the reluctance of the circuits through which those lines of magnetic flux pass which are produced by the primary current but which do not encircle the secondary.

We will make the assumption that lines of magnetic flux pass out of the portions of iron core which are not covered by primary windings, and leave the core in directions perpendicular to the surface. On this assumption, we will calculate the reluctances of the stray flux circuits emanating from those portions of the surface which are not covered with windings, and we will form the sum of their reciprocals.

We will use the following notation:

$\mathfrak{R}_{1a}$, the reluctance of the stray flux between AA and A^1A^1.
$\mathfrak{R}_{1b}$, the reluctance of the stray flux between BB and B^1B^1.
$\mathfrak{R}_{1c}$, the reluctance of the stray flux between AABC and $A^1A^1B^1C^1$.
$\mathfrak{R}_{1d}$, the reluctance of the stray flux between AC and A^1C^1.

It will be easily seen that the lines of magnetic flux which pass out of the core surfaces between the vertical sections CC^1 and $C_1C_1^1$ encircle the secondary, and therefore do not represent any stray flux.

The total stray flux reluctance, $\mathfrak{R}_1$, is then found from the equation,

$$\frac{1}{\mathfrak{R}_1} = \frac{2}{\mathfrak{R}_{1a}} + \frac{2}{\mathfrak{R}_{1b}} + \frac{4}{\mathfrak{R}_{1c}} + \frac{4}{\mathfrak{R}_{1d}} \tag{32}$$

We will *first* calculate $\mathfrak{R}_{1a}$ (Fig. 4). We suppose that the lines of flux are formed by two quarters of a circle connected by straight lines.

In considering a tube of flux of the thickness dx and width d, the reluctance of this tube will be

$$\frac{1}{d}\,\frac{\pi x + h}{d x}$$

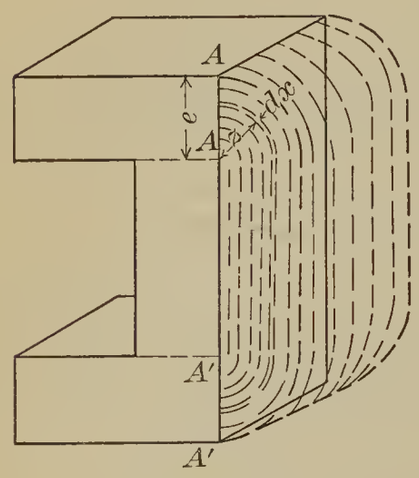


FIG. 4.

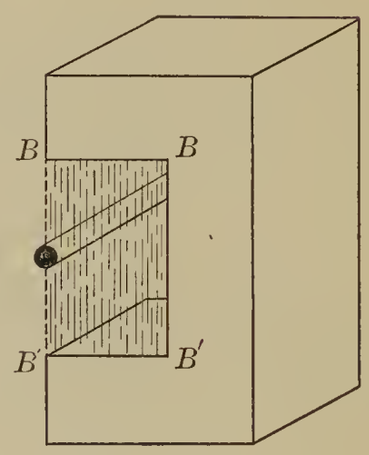


FIG. 5.

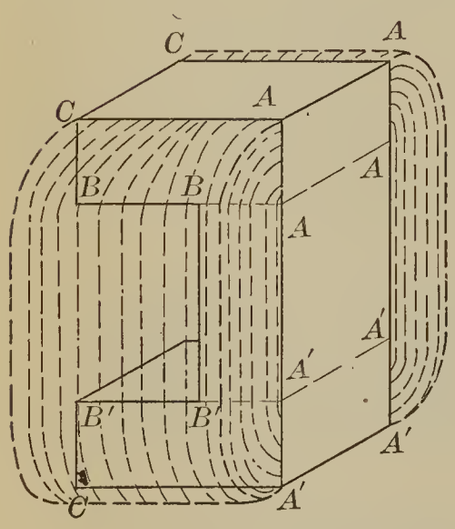


FIG. 6.

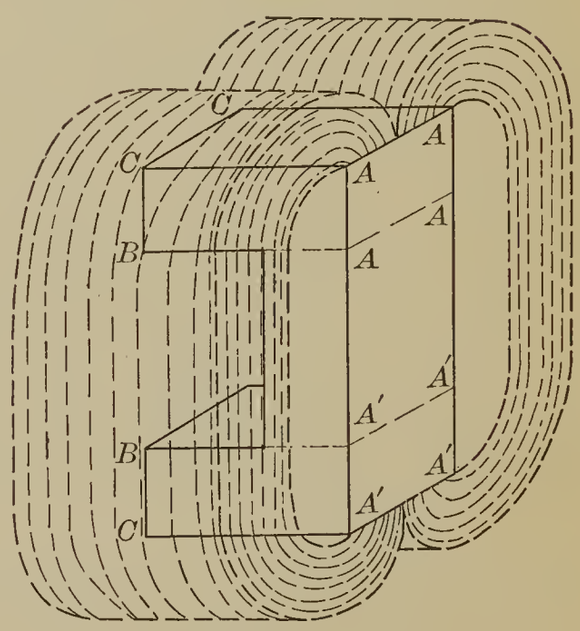


FIG. 7.

The total reluctance, $\mathfrak{R}_{la}$, will then be found from the formula,

$$\frac{1}{\mathfrak{R}_{la}} = d \int_0^e \frac{d x}{\pi x + h}$$

or

$$\frac{1}{\mathfrak{R}_{la}} = \frac{d}{\pi} \log \frac{\pi e + h}{h} \tag{33}$$

where "log" means natural or hyperbolic logarithms.

We will calculate *secondly,* the reluctance $\mathfrak{R}_{1b}$ (Fig. 5). The surfaces from which the lines of flux pass out are parallel and the distance between them is h. Since s is the area of each surface we get,

$$\mathfrak{R}_{1b} = \frac{h}{s} \tag{34}$$

or

$$\frac{1}{\mathfrak{R}_{1b}} = \frac{h^1 d}{2 h}$$

Thirdly, for calculating $\mathfrak{R}_{1c}$ (Fig. 6), we may use the same method for the calculation of $\mathfrak{R}_{1a}$, and find

$$\frac{1}{\mathfrak{R}_{1c}} = \frac{h^1 + 2 e}{2 \pi} \log \frac{\pi e + h}{h} \tag{35}$$

Fourthly, for calculating $\mathfrak{R}_{1d}$ (Fig. 7), we assume that the lines of flux have the form indicated in the illustration. We get

$$\frac{1}{\mathfrak{R}_{1d}} = \frac{1}{2} \int_0^{\frac{d}{2}} \frac{(h^1 + 2 e) d x}{\pi x + \pi (e + x) + h}$$

or

$$\frac{1}{\mathfrak{R}_{1d}} = \frac{h^1 + 2 e}{4 \pi} \log \frac{\pi (d + e) + h}{\pi e + h} \tag{36}$$

The formula (32) then assumes the form,

$$\frac{1}{\mathfrak{R}_1} = \frac{h^1 d}{h} + \frac{2 (d + 2 e + h^1)}{\pi} \log \frac{\pi e + h}{h} + \frac{h^1 + 2 e}{\pi} \log \frac{\pi (d + e) + h}{\pi e + h} \tag{37}$$

c. Calculation of $\mathfrak{R}_2$.—The flux produced by the secondary in the annular space which separates the two circuits may be calculated without taking account of the presence of iron. As a matter of fact, the secondary circuit is so far remote from the iron core that the lines of flux, which enter the iron at all, continue their passage through the iron core, and therefore encircle the primary.

This flux is of the form,

$$\varphi_2 = \int_0^{s_1} H \, d s$$

where S_1 is the section of the annular space under consideration, ds, an element of this section, and H, the field at the point of ds.

If we consider the flux through the surface $\alpha\,\beta\,\gamma\,\delta$ (see Fig. 3), neglecting the presence of iron, we get

$$(38) \qquad \varphi_2{}^1 = \int_0^{s_1} H\,d\,s + \int_0^{s_2} H\,d\,s$$

S_2 being the surface $\alpha^1\,\beta^1\,\gamma^1\,\delta^1$.

But $\int_0^{s_2} Hds$ is very small compared with $\int_0^{s_1} Hds$, because, first, S_2 is very small, compared with S_1, and second, it is small for the elements ds remote from the circuit.

If we neglect the influence of S_2, equation (38) becomes[4]

$$(39) \qquad \varphi_2 = \frac{4\,\pi\,n_2{}^2\,i_2}{\mathfrak{R}_2}$$

By adopting this value, a small error is committed, which will compensate for the error of neglecting the presence of iron. If L_2 is the self-induction of the secondary in air, calculated as though there was no iron, we get

$$\varphi_2 = L_2\,i_2$$

hence

$$(40) \qquad \mathfrak{R}_2 = \frac{4\,\pi\,n_2{}^2}{L_2}$$

If we apply for the determination of L_2 a method analogous to that of Mascart [Leçons sur l'Electricité et le Magnetism, 1896], we get

$$(41)\ L_2 = 4\left[a \log \frac{2\,a\,b}{r^1\,(a + \sqrt{a^2 + b^2})} + b \log \frac{2\,a\,b}{r\,(b + \sqrt{a^2 + b^2})} + 2\,(\sqrt{a^2 + b^2} - a - b)\right]$$

By inserting this value in equation (40), we get

$$(42)\ \mathfrak{R}_2 = \frac{\pi\,n_2{}^2}{a \log \frac{2\,a\,b}{r^1\,(a + \sqrt{a^2 + b^2})} + b \log \frac{2\,a\,b}{r\,(b + \sqrt{a^2 + b^2})} + 2\,(\sqrt{a^2 + b^2} - a - b)}$$

[4] NOTE OF TRANSLATOR:—While the reactive electromotive force for a certain value of current varies with the square of the number of turns (see equation 6), the leakage flux itself varies directly with the number of turns. In equations (39), (40) and (42) n_2 should be therefore substituted for $n_2{}^2$ in the numerator.

NOTE.—For the calculation of $\mathfrak{R}_2$ we have assumed that the whole flux produced by the secondary, and passing through the inner vertical legs of the iron core, will remain in the iron and encircle the primary. It is more exact to assume that the lines of flux produced by the secondary, and passing through the central legs of the iron core, come from all directions, and follow in their path the primary stray fluxes.

The reluctance $\mathfrak{R}_2$ should therefore be combined with the reluctance $\mathfrak{R}_1$. If $\mathfrak{R}_2$ is the reluctance calculated from (42), and $\mathfrak{R}_2^1$ the real reluctance, we get

$$\frac{1}{\mathfrak{R}_2^1} = \frac{1}{\mathfrak{R}_2} + \frac{1}{\mathfrak{R}_1} \tag{42 a}$$

2. *Second method: Primary windings placed on upper horizontal arms.*—We will now assume that the primary windings

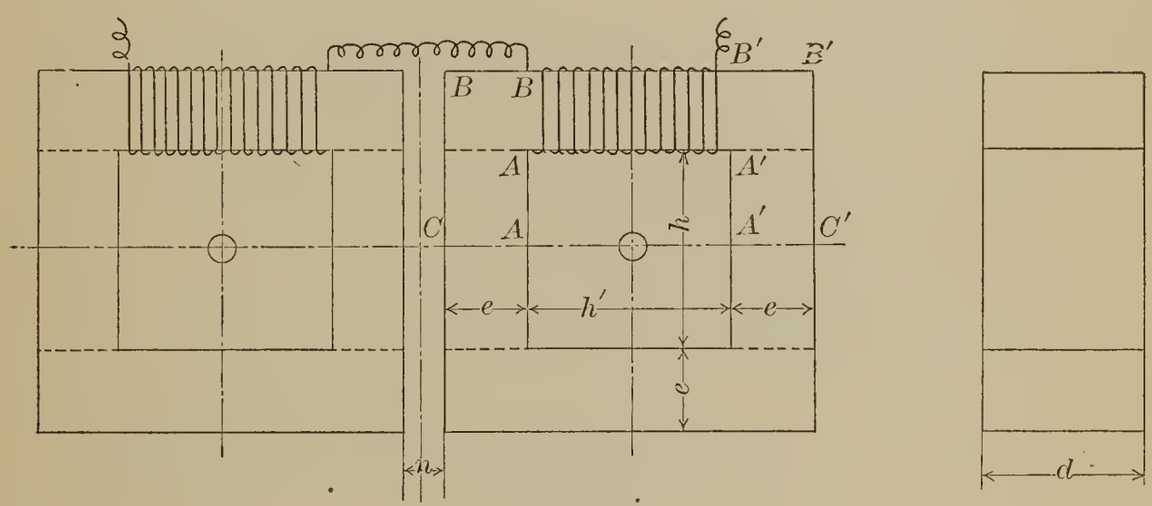


FIG. 8.

are placed on the upper horizontal arms of the iron cores, and outside of the furnace.

a. As to the calculation of $\mathfrak{R}$, this has the same value as in the preceding case,

$$\mathfrak{R} = \frac{1}{2\,\mu\,s} = \frac{h + h^1 + e}{\mu\,d\,e} \tag{31}$$

b. For the calculation of $\mathfrak{R}_1$, we will make again the same hypothesis as in the first case, and calculate separately the different stray fluxes. We use the following notation:

$\mathfrak{R}_{1a}$ is the reluctance of the stray flux cicuit between AA and A^1A^1.

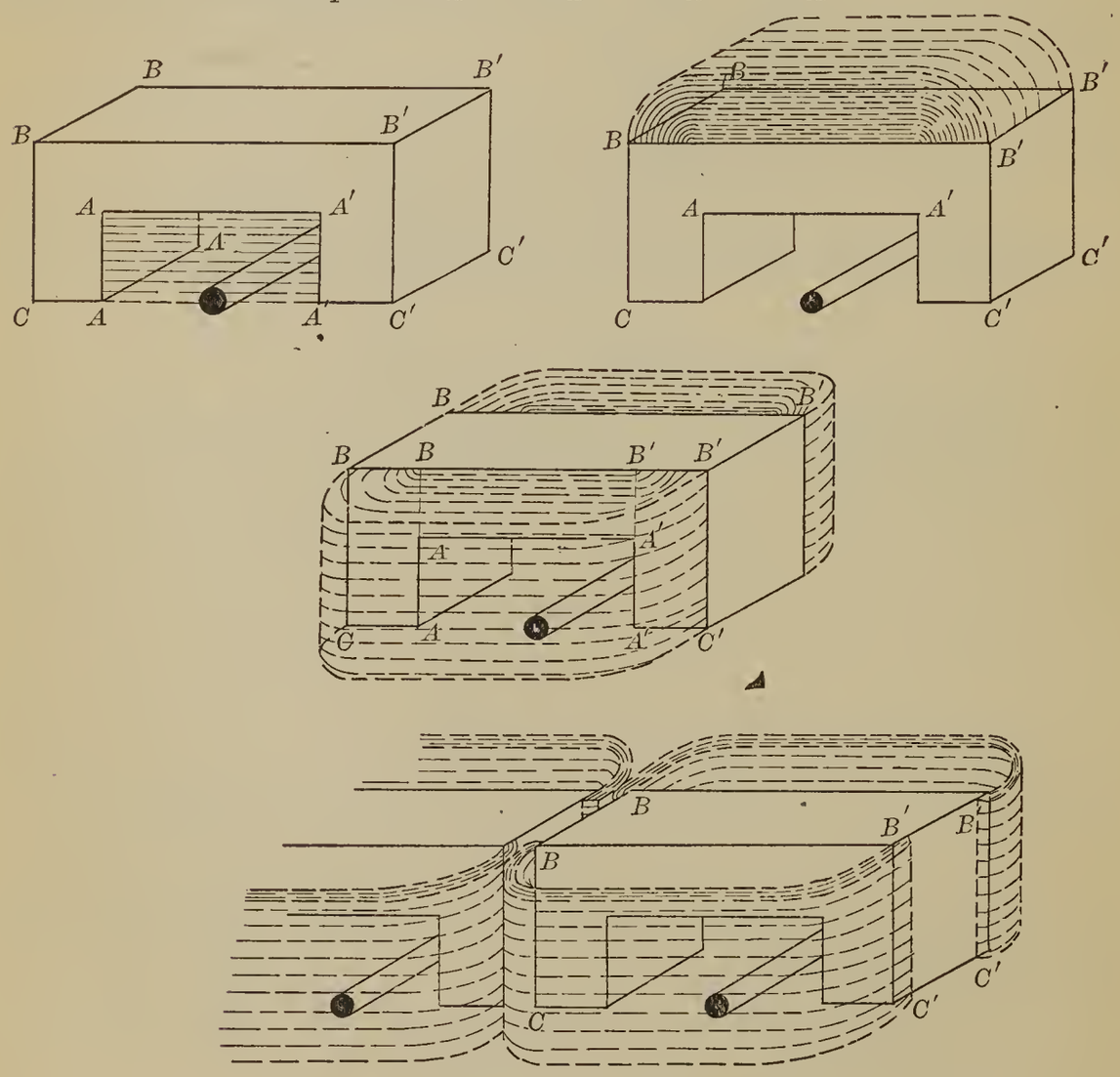
$\mathfrak{R}_{1b}$ is the reluctance of the stray flux circuit between BB and B^1B^1.

$\mathfrak{R}_{1c}$ is the reluctance of the stray flux circuit between ACBB and $A^1C^1B^1B^1$.

$\mathfrak{R}_{1d}$ is the reluctance of the stray flux circuit between BC and B^1C^1.

Further, we have

$$\frac{1}{\mathfrak{R}_1} = \frac{2}{\mathfrak{R}_{.a}} + \frac{2}{\mathfrak{R}_{1b}} + \frac{4}{\mathfrak{R}_{1c}} + \frac{4}{\mathfrak{R}_{1d}} \tag{43}$$



Figs. 9, 10, 11 and 12.

Firstly, for calculating $\mathfrak{R}_a$ (Fig. 9), the formula (34) gives

$$\mathfrak{R}_{1a} = \frac{h^1}{\frac{h}{2}\,h} = \frac{2\,h^1}{h\,d} \tag{44}$$

Secondly, for calculating $\mathfrak{R}_{1b}$ (Fig. 10), we get, by means of formula (33),

$$\frac{1}{\mathfrak{R}_{1b}} = \frac{d}{\pi} \log \frac{\pi\,e + h^1}{h^1} \tag{45}$$

Thirdly, for calculating $\mathfrak{R}_1$ (Fig. 11), we get from formula (35),

$$\frac{1}{\mathfrak{R}_{1c}} = \frac{h + 2e}{2\pi} \log \frac{\pi e + h^1}{h^1} \tag{46}$$

Fourthly, for calculating $\mathfrak{R}_{1d}$ (Fig. 12), we get, by formula (36),

$$\frac{1}{\mathfrak{R}_{1d}} = \frac{h + 2e}{4\pi} \log \frac{\pi (e + n) + h^1}{\pi e + h^1} \tag{47}$$

The formula (43) then assumes the form,

$$\frac{1}{\mathfrak{R}_1} = \frac{hd}{h^1} + \frac{2(d + h + 2e)}{\pi} \log \frac{\pi e + h^1}{h^1} + \frac{h + 2e}{\pi} \log \frac{\pi (e + n) + h^1}{\pi e + h^1} \tag{48}$$

c. Calculation of $\mathfrak{R}_2$.

The value of $\mathfrak{R}_2$ is given by formula (42), and has no additional terms, as in the case of the windings around the outer vertical legs.

The comparison of the final formulas shows that it is preferable to place the primary winding on the upper horizontal arms of the cores, instead of placing them on the outer vertical legs.

It is also easy to see that it is preferable to connect the two windings in series, and not in parallel.

DISCUSSION.

Dr. E. F. Roeber: Mr. Gin has certainly done a useful work in giving for the first time a mathematical theory of the induction furnace, which now attracts so much attention in metallurgy. If I am permitted to say a few words about his theory, the starting point of the same undoubtedly is correct in principle. From the viewpoint of scientific economy, however, it seems to me injudicious to start from the fundamental differential equations of alternating current engineering in order to get at the equations of the induction furnace. The way is so long that many hypotheses are required. Indeed, Mr. Gin's calculation of the stray fluxes seems more or less guesswork. I don't want to say anything against Mr. Gin's equations for the stray fluxes. They

may be all right, but we cannot say so from the way in which they are derived. The possibility of representing the stray fluxes by Mr. Gin's equations will have to be proven experimentally; then the equations will be empirical, and if we have to use empirical formulas, it might be possible to render them simpler. On the whole, Mr. Gin's mathematics seem too complicated to recommend itself as a working theory to a furnace man. A much better starting point to get a working theory of the induction furnace seems to me to start from the theory of the induction motor which has been worked out in detail and is known to represent the facts correctly for the motor. Now, the induction furnace and the induction motor are special cases of the general alternating current transformer and have in common the large magnetic leakage—which distinguished them from a well designed ordinary transformer. It would seem that whole parts of the theory of the induction motor could be taken over bodily to serve as a working theory of the induction furnace. Experiment would have to show, of course, how far we could go in this respect.

Mr. Carl Hering: Is there any benefit in putting the coils on the top instead of on the bottom? I should think you would want to keep the top as free as possible from copper wires.

Dr. Roeber: To put the windings on the top—on the horizontal upper arms—seems to have mechanical advantages.

Mr. Hering: You get the heat from the top of the furnace there, whereas at the bottom you can insulate for heat better.

Dr. Roeber: Mr. Gin considers only these two cases: putting the windings on the outer vertical legs or putting them on the upper horizonal legs, and from his formulas, which are based more or less on guesswork, he finds that the latter arrangement is more efficient.

Prof. Jos. W. Richards: If that efficiency was really attainable, the radiation could be cut off entirely by means of a water jacket or shield, which will protect this entirely from the radiation; but I should rather think they would be more in the way of the working of the furnace than if placed underneath. Aluminium wire can be oxidized superficially, and then wound into a coil without any insulation other than the film of oxide. This will stand some considerable voltage without puncturing, and would be quite unaffected by any heating which it would get by radiation from the furnace.

Mr. Hering: Wire is being made now for just such purposes, which is covered with asbestos. I tested some coils of this wire, which were heated to almost a red heat, and found the insulation remained good. The difficulty is not so much with the insulation of the copper; it is the iron that will give trouble. Iron at a red heat becomes non-magnetic.

In connection with the induction furnace, some interesting points arise with reference to the attempted measurements of the drop of potential in the trough. I call attention to them here because it seems that the principles underlying the measurement of the drop of potential or the e. m. f., are not always clearly understood, thereby leading to erroneous conclusions. When a dynamo supplies current to an external circuit, the voltage is produced entirely in the armature of the dynamo, and the corresponding drop of potential is all in the external circuit (neglecting the small drop of potential in the armature itself). It therefore becomes possible to measure each separately. In a short-circuited secondary of a transformer, however, the conditions are different, as the induction of the voltage takes place in the same conductor in which the corresponding drop of potential occurs, due to the current passing through the resistance. It would therefore lead to entirely erroneous conclusions to measure the drop of potential in the trough of an induction furnace, even if such a measurement could be made. The conditions are analogous to a ball rolling continuously around a circular groove, but rolling down hill all the time; this becomes possible by assuming some such explanation as that the ball rolls down infinitely short inclined planes, and that by some external force these inclined planes are continually being raised as the ball rolls down, the general level of the circular groove therefore remaining the same. I call attention to this particular case, as I understand attempts have been made to measure the drops of potential in the trough of an induction furnace, and to measure electrolytic conductivity by the drop of potential in such a trough filled with an electrolyte.

In this connection it naturally suggests itself to measure the e. m. f. by breaking the circuit in the trough of an induction furnace by inserting a slab of insulating material; there will then be no current flowing and therefore no drop of voltage, but, even

in this case, the measurements would lead to entirely erroneous results. This will be seen from the two adjoining figures in which T is the trough of the induction furnace which is broken at B; the iron core is represented by C, and the voltmeter by V. When the leads are applied as shown in Fig. 1, they will measure the total voltage as induced in the trough. But, if these leads be now moved along the trough towards the other side, as shown by the dotted lines, it seems that the voltage measured would continue to remain the same, therefore leading to the erroneous conclusion that the total voltage was generated in that short section *a*, at the other side of the trough. But that this is erroneous would be shown by the fact that if the leads are now removed from the trough and connected together, the voltage indicated by the voltmeter will stay the same. The explanation of this is that the voltage measured is partly, or in the latter case

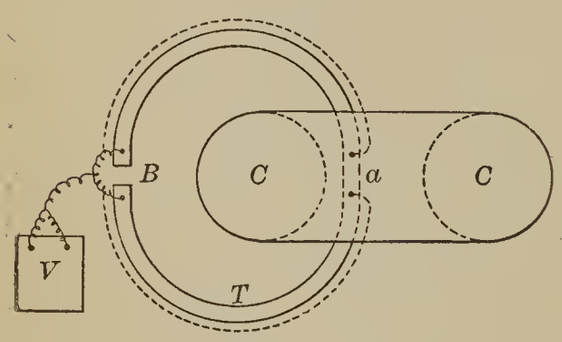


FIG. 1

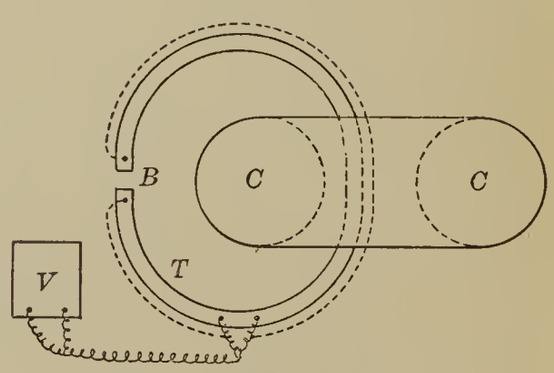


FIG. 2

entirely, induced in the leads of the voltmeter. It is here assumed that the voltmeter leads follow the trough closely; if not, there would be a slight difference due to the magnetic leakage in the area enclosed by the voltmeter leads and the trough.

Similar erroneous results will be obtained if the voltmeter is connected as in Fig. 2, and the points of application be then moved along the trough until they reach the position shown in the dotted lines. The difference in Fig. 2 and Fig. 1, however, will be that in Fig. 2 there will be no voltage indicated by the voltmeter in all three positions. The explanation is that the induction in the leads and in the trough are, in this case, in opposite directions, thus neutralizing each other.

It will thus be seen that such measurements lead to entirely erroneous results, owing to the induction in the leads, and that it

seems impossible to get rid of this induction. The above is based entirely on theory, and it would be interesting to have it confirmed by an actual test, which could readily be made by placing a cut copper ring around one core of a transformer.

PROF. RICHARDS: Suppose the instrument were placed near to the wires, the two of which are perpendicular to the plane of the secondary, so that they do not in any case encircle the secondary, or in other words, the leads were taken perpendicularly from that plane to the instrument?

MR. HERING: I think it will be found that no matter how the leads are run, it is not possible to make the measurement.

MR. GEORGE BREED: I think Mr. Hering's diagram is intended to show the voltmeter wires enclosing the magnetic circuit. If you were to remove the break in the secondary circuit and place it on the other side, you would have the case where you would get no circuit, because you have two circulations of the magnetic circuit in opposite directions.

MR. HERING: I fear you cannot possibly arrange them bifilar. You say that the voltage can be calculated in them. If the wires are very near to the trough no calculation is necessary, because there would be the same induction as the middle of the trough; the only difference between the two would be that due to leakage between the wire and the trough; for this reason it would be a very difficult calculation to make.

A paper read by Dr. Jos. W. Richards at the Twelfth General Meeting of the American Electrochemical Society at New York City, October 18, 1907; President C. F. Burgess in the chair.

THE ELECTROMETALLURGY OF ZINC.

By Gustave Gin.

(Translated by Jos. W. Richards and W. S. Landis.)

GENERAL OBSERVATIONS.

Before taking up the study of the electrometallurgy of zinc it will be useful to first discuss the imperfections of present methods in order to deduce the possible or desirable improvements.

As is well known, the reduction of oxide of zinc is done solely in closed vessels by means of carbon, at a temperature above 1000°. The zinc is thus reduced and vaporized; there is formed also CO gas, which likewise reacts on the oxide of zinc, forming CO_2 gas. To prevent this CO_2 gas from reoxidizing the vapor of zinc, there is placed an excess of carbon in the mixture to be reduced; under these conditions CO_2 gas is transformed by this excess of carbon into CO, which reduces again zinc oxide, and again passes through the same series of transformations. In practice, in spite of the excess of carbon used, it is impossible to prevent the partial re-oxidation of the zinc.

We may remark also that the heat of the furnace has to transverse not only the sides of the vessel, but also the whole of the material to be heated. To obtain the high temperature necessary for the reduction, the capacity of the distilling vessels must necessarily be restricted and their sides made very thin. The manufacture of these vessels of limited thickness and therefore limited strength necessitates a considerable expenditure of hand labor, and of combustible in their drying and annealing. The setting of these retorts and their replacement are likewise onerous. The necessity of having these vessels as permeable as possible to heat results in giving their sides a minimum thickness, which leads to their cracking and the consequent loss of metallic vapors.

The necessity of keeping the reducing retort at a high temperature while the condensers are on the contrary cool, implies a relatively thin wall to the furnace, and, in consequence, a considerable loss of furnace heat. Since on the other hand the methodic scheme of heating is impossible, we are face to face with very poor conditions for obtaining satisfactory thermal efficiency.

In spite of all the efforts of metallurgists it has not been possible to improve upon the essential principles of the metallurgy of zinc, and no one has yet succeeded in reducing zinc ores and condensing the metal to the liquid state in a cupola furnace. The only improvements which have been brought into practice have been the introduction of heating by gas, a more rational use of refractory materials for distilling retorts, the increased size of the furnace, and improvements in the condensation of the zinc vapors. In spite of these improvements, it is estimated that the losses of zinc are still 8-12 per cent. in the Belgian method and 10-20 per cent. in the Silesian method, distributed as follows:

	Belgian Practice	Silesian Practice
(1) Incomplete distillation	5–8 per cent.	8–15 per cent.
(2) Absorption by retorts and condensers . .	1 " "	1 " "
(3) Incomplete condensation	2–3 " "	2–3 " "

In conclusion, the inconveniences of present practice may be stated as follows:

Great expense of fuel, labor and distillation apparatus.

Discontinuity of operation.

Unfavorable extraction-losses of 10-20 per cent. of the metal contained in the ore.

We have been speaking only of the reduction of oxidized material, but we should speak likewise of the direct reduction of sulphide ores, which has up to the present not been accomplished. The reaction of the oxide of zinc upon its sulphide has been tried, but takes place only at very high temperatures, and the SO_3 gas produced reacts upon the zinc vapor during distillation and condensation. On the other hand, the action of carbon upon zinc sulphide is possible at very high temperatures, but the reaction is likewise reversible. Reduction by iron has been likewise tried, but it takes place at a temperature too high to be utilized in closed vessels; further, it appears impossible to obtain intimate contact

between the ore and the particles of iron. Finally, the simultaneous reaction of lime and carbon upon zinc sulphide has been proved in the laboratory, but has never been tried industrially.

Such was the state of the art before serious researches were taken up in the electrometallurgical way.

ELECTROMETALLURGICAL PROCESSES.

The imperfections in the metallurgy of zinc have led to numerous researches on the electrical extraction of the metal. These attempts were at first in the electrolytic line, but after several attempts in this direction had proved unsuccessful, investigators turned towards reduction by igneous methods in the electric furnace.

In the line of electrolysis in the wet way, we mention the work of Luckow, Letrange, Blast and Miest, Hermann, Squire and Currie, Siemens and Halske, Nahnsen, Kiliani, Lange and Kosmann, Coehn, Cowper-Coles, Pfleger, Hoepfner, Tossizza, Borchers, Ashcroft.

The process of Ashcroft had been especially worked out for the treatment of the complex ores of Broken Hill. It was based on the chloridizing action of perchloride of iron, which transformed the zinc of the ores into a solution which was capable of being electrolyzed. The losses of zinc were too large and the increasing volume of solutions required too expensive a plant. The process was installed at Newcastle, N. S. W., but has been abandoned.

The Hoepfner process was the outcome of long study by its author at Iührfurt on the Lahn. It has been taken up lately by the firm of Brunner & Mond, which is now producing electrolytic zinc 99.9 per cent. pure in its works at Wilmington, near Chester, England.

Swinburne has likewise experimented on a process for the chloridizing of zinc and the fusion and electrolysis of the melted chloride.

In the electrothermic line we may mention the investigations of Dorsemagen (French Patent, No. 178,535), Salgues (French Patent, No. 310,100, 380,665), Casaretti and Bertani (French Patent, No. 295,971), Danckwart (American Patent, No. 746,798), Gin (German Patent, No. 169,208), Society of Elec-

trical Energy of Trolhättan, System Laval (French Patent, No. 325,895).

Up to the present the last two processes are the only ones which have given encouraging results. The process of Laval furnishes a commercial zinc marked G. D. L., and of a purity comparable to that of the Sterling and Vieille Montagne Extra Pure A brands. It seems that this purity can be otherwise obtained only by a double distillation of crude zinc.

THE NEW PROCESS OF GIN.

The first furnace of the author was an electric furnace having electrodes, but the difficulties in using the electrodes in a closed vessel were so great that efforts were made to adopt the induction furnace to this purpose.

The induction furnace in use up to the present consists of a circular crucible which surrounds a closed magnetic circuit which carries a winding forming the primary coil, while the circular crucible containing the material to be treated constitutes the secondary coil, of one single turn. On passing an electric current through the primary circuit there is induced in the secondary another electric current whose energy is there transformed into heat. This transformation into heat may be accomplished either in the material which it is desired to heat or in a conductor in contact with this material. The process and the special furnace of the author for the electro-thermic treatment of zinc ores are based on the application of this last method of heating, using as the seat of the Joule effect a material capable of reacting chemically on the material to be treated.

To go more at length into the principles and extent of the invention, suppose that in the channel of the induction furnace there is placed a metal in the state of fusion. Any material put in contact with this metal will be decomposed if it is able to form with the same another compound more exothermic than the first. It is thus possible with a given metal to set other metals at liberty. If the metal set free is capable of alloying with the first their alloy will result. If the metal set free is volatile it can be collected by condensation. This is the case when zinc oxide and sulphide are reduced by iron at a temperature above 1300°.

It is equally possible to limit the action of the iron to that of a

conductor and producer of heat, and to utilize this heat to provoke reducing reactions in the mixture of carbon and metallic oxide or silicate, or of carbon, lime and metallic sulphide.

Principles of the Circulating Induction Furnace of Gin.

In the induction furnace it is difficult because of the low calorific conductibility and the slowness of diffusion of the melted bodies to obtain uniform distribution of the heat generated and uniform reaction. An industrial effect much more perfect obtained by continuously circulating the melted material results in a uniform mixture in all other parts and an incessant changing of the surface of contact of the liquid and solid materials in the furnace.

The author obtains this circulation by using as his crucible a series of channels, the bottoms of which are inclined longitudinally, the deepest part of each being connected by a conduit with the more shallow part of the next channel. The channels have a relatively large section so that the fused material, while filling completely the conduits or connections from one channel to another, only occupies a part of the sections of the channels themselves.

The quantity of electric energy transformed into heat varies inversely with the section of the conductor; the molten mass is for this reason cooler in the top parts of the channels than in the other extremity. By reason of the difference of temperature, and consequently of density, there results an ascensional movement of the liquid in the connecting conduits, reinforced by the further heating in the conduit itself, and by reason of this produces a general circulation throughout the whole mass, forming the secondary circuit.

The Gin Furnace for the Manufacture of Zinc.

The author uses the principle patented by him in the above described induction and circulating furnace for the treatment of oxides and of sulphides of zinc. Figs. I, II, III are vertical sections of this furnace, Fig. IV a horizontal section.

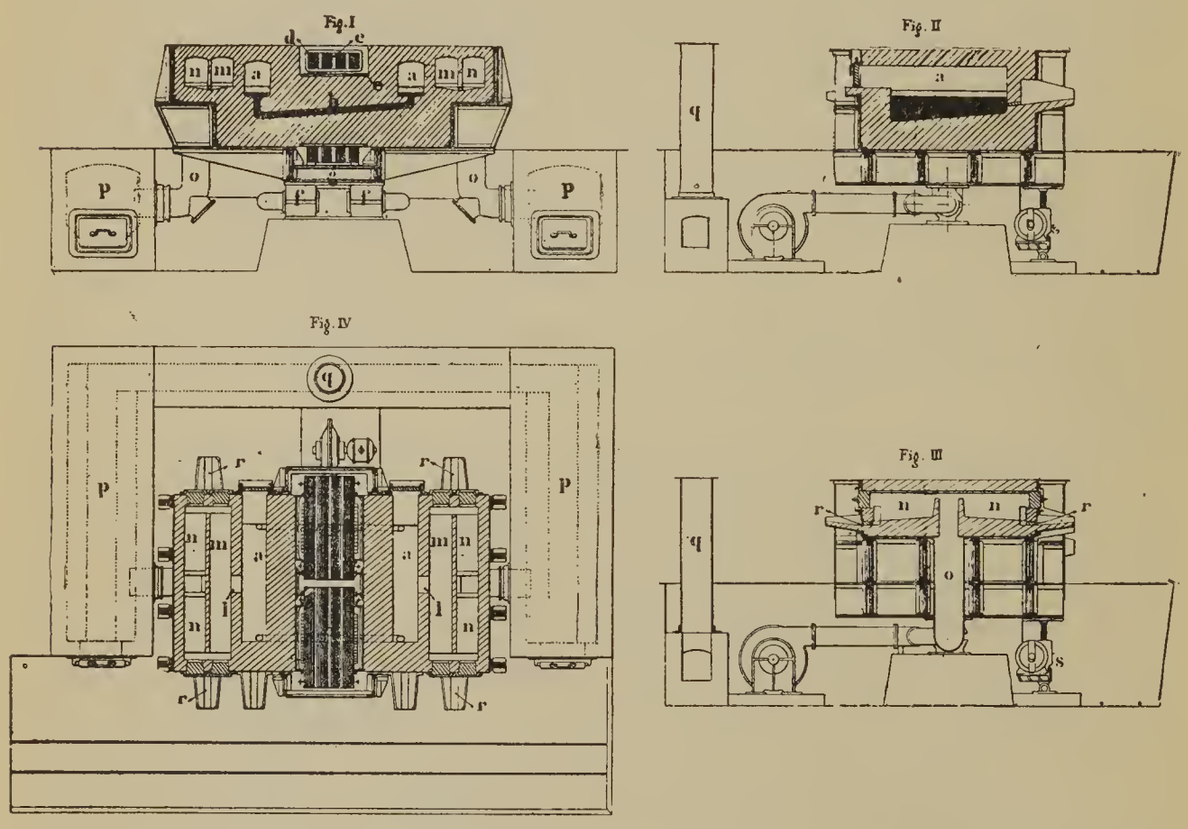
The channels with exposed surface, called the working channels (a), are placed parallel to each other, their bottom longitudinally inclined and united to conduits (b) of circular section, called the

heating conduits, which have the lower parts of each channel in connection with the more shallow parts of the following channel.

The primary circuit is composed of an insulated copper coil around the upper horizontal branches of the double magnetic circuit (cc). The two coils constituting the primary (dd) have the same number of turns and are connected in series.

The secondary circuit is constituted by the bath of liquid iron contained in the channels (a) and the conduits (b).

To protect the conducting cables from the radiation of the hot masonry there is interposed between the inside faces of the mag-



netic coil and the adjacent masonry, metallic channels (e) cooled by a current of water. The masonry does not rest directly on the lateral faces of the inductor, but is supported on plates which themselves rest on pins. The water for cooling passes between these plates and the inductors.

A fan is used to send a current of air around the magnetic core and the primary winding, so as to keep them cool. The air is led in through trunnions (f) and is distributed by the boxes (g). Dampers, movable by chains, pullies and an endless screw, permit a regulation of the circulating air and its proper distribution. The

whole furnace is contained in a sheet iron shell resting upon two trunnions (f).

The lining of the furnace is formed of burnt dolomite, agglomerated by pitch and stamped in like the hearth of the Siemens-Martin furnace. The roof is made of bricks of burnt magnesite, the contraction of which is practically nothing.

The bath of iron being at a suitable temperature, there is spread upon its surface by a charging device, similar to that used for charging gas retorts, a mixture of the oxide of zinc and carbon or of the sulphide, lime and carbon. When the charging is done, the working door is quickly closed and the joints plastered up with clay to prevent the entrance of air. Continuing the heating the temperature of the mixture is raised rapidly and the distillation of the zinc commences.

Zinc vapor and the oxide of carbon escape from the working channel by the orifices (l) and pass to the condensing chambers (m) and (n). In the chamber (m) the mean temperature is normally about 500°, but below 700°, so that the condensation to the liquid state takes place easily upon its upper wall and upon the wall opposite to the point of entrance of the vapors; the uncondensed vapors are finally brought down in the chamber (n). Any zinc oxide and dust carried along by the carbon monoxide pass along into the conduit (o) and are deposited in the dust chambers (p) which connect with a common chimney (q).

When the reduction is finished the condensed zinc is run out by opening the tap hole (r) and inclining the furnace to one side by means of the motor-driven jack-screw (s).

Finally the residues are scraped out of the working door by the use of a metallic rabble.

The heating is not interrupted during the tapping of the zinc or the cleaning out of the residue, so that one-half at least of the furnace is always active.

The circulating induction furnace provides a perfectly closed space in which the heating is effected, and not through a wall or partition as in the present furnace, but by direct contact of the mixture to be reduced with the metal in which the Joule effect is produced. Besides, the mixture with carbon, especially when it contains blende which is conducting, is of itself the seat of the development of electric heat to a not unimportant degree.

It is therefore possible with this electrothermic heating to use distillation capacity as great as one wishes, this capacity being limited only by the power of the electric furnace. At the same time the expense of refractory material is very much reduced, the hand labor is less than in the old furnace with the small muffles, and finally the loss of metal by incomplete reduction, by cracking of retorts, by reoxidation and imperfect condensation, is reduced to a minimum, far below that obtained in a furnace heated by coal or gas.

Estimate of the Economic Value of This Process.

The value of a process may be practically deduced from the cost of production. In the case of the electrothermic manufacture of zinc, the principal factor in the cost being the expense for electric energy, we will fix in the first place the consumption of energy required for the production of a ton of zinc. We will investigate afterwards the other elements of cost, general expenses, labor, maintenance, depreciation, etc. For the valuation of these costs, which are not proportional to the production of metal, it will be necessary to make further on an estimate in relation to the size of the works.

Energy to Reduce Zinc Compounds.

To calculate the heat necessary for the physical changes and chemical reactions we will suppose that the reactions take place at zero, and that the products of these reactions are then carried up to the temperature at which they leave the furnace.

As an example, we will take the most simple reaction, the reduction of zinc oxide according to the equation

$$ZnO + C = Zn + CO.$$

The calculation of the heat necessary for the reduction of a kilogram-molecule would be as follows:

A—Net heat of formation.

Initial state.....	$ZnO + C$ = 84,800 cal.	
Final state.....	$CO + Zn$ = 29,400 "	
		55,400 cal.

B—Heat in the products.

From 0°—420°	420 × 6.5 =	2,730 cal.	
Latent heat of fusion	=	1,820 "	
From 420°—920°	500 × 8 =	4,000 "	
Latent heat of vaporization	=	15,370 "	
From 920°—1200°	280 × 10 =	2,800 "	
Gas from 0°—1200°	1200 × 6.9 =	8,280 "	
			35,000 cal.

Total calories consumed.....90,400

Total calories consumed per ton of zinc, 1,390,000.

Electric furnaces have a thermal efficiency quite high, and we may assume, in the following calculation, that such furnaces will give us a thermal efficiency of 65 per cent. In the above case, this will correspond to an expenditure of 2,472 kilowatt-hours per ton of zinc.

Calculating in the same manner the energy required for the other principal compounds of zinc, we have the following table:

Ore.	Reaction.	Energy required in Kilowatt-hours.
Oxide	$ZnO + C = Zn + CO$	2,472
Carbonate	$ZnCO_3 + 2C = Zn + 3\,CO$	4,330
Silicate	$ZnSiO_3 + C = Zn + SiO_2 + CO$	3,830
	$ZnSiO_3 + CaO + C = Zn + CaSiO_3 + CO$	4,000
Sulphide	$ZnS + CaO + C = Zn + CaS + CO$	2,965

Because of the relatively high cost of electric energy, it is advisable to previously calcine the ore, in order to transform the carbonate of zinc into oxide. This operation is still more advantageous when the carbonates are hydrated, for a part of the electric energy would be used for vaporizing the combined water, and there would be an extra consumption of carbon because of the partial decomposition of the water vapor.

It is well recognized, in electrothermal applications, that the function of the electric current should be restricted as far as possible to the sole uses in which it is indispensible or for which it is clearly superior to the use of other kinds of energy.

Energy Necessary to the Reduction of Calcined Calamine.

Before taking up the reduction of the pure compounds of zinc, we will discuss the reduction of calcined calamine, the ore containing:

ZnO	40.50	Zn ..... 50.05 per cent.
$ZnSiO_3$	38.07	
Fe_2O_3	9.60 per cent.	
Al_2SiO_5	8.10 " "	
Diverse	3.73 " "	

It may be expressed in a chemical formula as

$$5ZnO + 2.7ZnSiO_3 + 0.6Fe_2O_3 + 0.5Al_2SiO_5 + 0.1CaO,$$

which expresses the number of kilogram-molecules of the material contained in a ton of substance treated. Including the loss, the consumption of energy may be determined according to the following equations, in which the proportions of CaO and C are calculated so that only a small part of the iron will be reduced.

For one ton of calcined mineral represented by the preceding formula, there will be necessary 1.7CaO (95.2 kg.), and 8.6C (103.2 kg.). There will be formed by the reaction 7.7Zn (504.3 kg.), 0.3Fe (16.8 kg.), 8.6CO (240.8 kg.), and the slag, consisting of $0.5Al_2SiO_5$, $2.7SiO_2$, 1.8CaO, 0.9FeO (401.6 kg.).

(a) Heat balance of the above reaction:

Initial state	ZnO	$5 \times 84{,}800 = 424{,}000$	
	$ZnSiO_3$	$2.7 \times 284{,}400 = 767{,}880$	
	Fe_2O_3	$0.6 \times 197{,}000 = 118{,}200$	
	Al_2SiO_5	$0.5 \times 586{,}000 = 293{,}000$	
	CaO	$1.8 \times 145{,}000 = 261{,}000$	
			1,864,080 cal.
Final state	Al_2SiO_5	$0.5 \times 586{,}000 = 293{,}000$	
	$CaSiO_3$	$1.8 \times 344{,}400 = 619{,}920$	
	$FeSiO_3$	$0.9 \times 254{,}600 = 229{,}140$	
	CO	$8.6 \times 29{,}400 = 252{,}840$	
			1,394,900 cal.

Balance of the heat of reaction.....469,180 cal.

(b) Sensible heat in the products:

ZnO	— 1200°	7.7 × 26,720 =	205,744
Fe	— 1700°	0.3 × 22,400 =	6,720
Slag	— 1500°	401.6 × 460 =	184,736
CO	— 1200°	8.6 × 9,200 =	79,120

Total sensible heat in the products.....476,320 cal.

Total thermal requirement.....945,500 cal.

This amount of heat represents per ton of zinc 1,900,000 calories, and for a furnace of 65 per cent. efficiency, and losing 5 per cent. of the zinc content of the material treated, an energy requirement of 3,560 kilowatt-hours per ton of zinc obtained.

Energy Requirement for the Reduction of a Sulphide Ore.

Suppose a blende to have the following composition:

$$8ZnS + FeS + 2.2SiO_2,$$

expressed in kilogram-molecules per ton, or expressed in percentage, as:

Zn	52.00	per cent.
Fe	5.60	" "
S	28.80	" "
SiO_2, etc.,	13.60	" "

The expenditure of energy would be calculated from the equation:

$$8ZnS + FeS + 2.2SiO_2 + 10.2CaO + 8C = 8Zn + FeS + 8CaS + 2.2CaSiO_3 + 8CO.$$

This requires to a ton of ore 571.2 kg. lime and 96 kg. carbon, and forms 523.2 kg. zinc, 919.2 kg. slag, and 224 kg. carbon monoxide.

(a) Heat balance of the above reaction:

Initial state	ZnS	8 × 43,000 =	344,000	
	FeS	1 × 24,000 =	24,000	
	SiO_2	2.2 × 179,600 =	395,120	
	CaO	10.2 × 145,000 =	1,479,000	
	Total			2,242,120 cal.
Final state	FeS	1 × 24,000 =	24,000	
	CaS	8 × 104,300 =	834,400	
	$CaSiO_3$	2.2 × 344,400 =	757,680	
	CO	8 × 29,400 =	235,200	
	Total			1,851,280 cal.
	Heat balance of reaction			390,840 cal.

(b) Sensible heat in products:

Zn to 1200°	8 × 26,720 =	213,760	
Slag to 1500°	919.2 × 460 =	422,832	
CO to 1200°	8 × 9,200 =	73,600	
Total sensible heat			710,192 cal.
Total energy requirement			1,101,032 cal.

This equals for a ton of zinc 2,117,300 calories, and for a furnace of 65 per cent. efficiency, and losing 5 per cent. zinc contents of the ore, 3,960 kilowatt-hours per ton of zinc obtained.

Treatment of Complex Sulphide Ores.

When the ores contain a large proportion of galena and sulphide of iron the method of treatment would remain the same, but would require supplementary operations. If the proportion of iron is considerable, it may be of advantage to submit the mineral to magnetic concentration before sending it to the electric furnace, but all ores are not equally amenable to this process.

Argentiferous Sulphides.

When the blend contains sufficient silver to make it desirable to extract the precious metal, iron is not to be recommended as the heating agent in the electric furnace; nickel, copper or lead

should be substituted for it. If iron alone is used, the lead separated out absorbs the silver and sinks to the bottom of the heating channels. But the temperature of this region being hotter than that of the mixture being reduced, and above the boiling point of lead, this metal is vaporized, and its silver absorbed by the iron. The refining of an alloy of silver and iron is not a possible industrial operation. Bessemerizing this alloy volatilizes the silver, and its solution in a chemical way or by electrolysis would be very expensive.

The argentiferous lead, however, which shows no tendency to unite with cast iron, may be separated from the latter by the following device.

The bottom of each channel may be made to communicate by a small siphon with an external pocket open to the air, and into which the lead flows and from which it can be ladeled out. It is cupelled to extract the silver.

If nickel is used, which would be somewhat expensive, silver may be separated from it by a simple liquation.

If copper were used, the silver would remain alloyed with it in the furnace. When it is sufficiently rich, it may be cast into anodes and electrolyzed. The presence of iron in the ore to be reduced interferes with the use of copper as a collecting agent, since iron alloys with copper and interferes with the subsequent refining.

Application to a Complex Silver Ore.

Assume a complex blende analogous to the ores of Broken Hill, of the following composition:

Zn	26.00	per cent.
Pb	22.75	" "
Fe	8.40	" "
S	21.12	" "
Rhodonite	6.55	" "
Garnet	13.98	" "
Diverse	1.20	" "

and containing per ton of mineral the number of kilogram-molecules corresponding to the following formula:

$$4ZnS + 1.1PbS + 1.5FeS + 0.3(3SiO_2.\ Al_2O_3.\ FeO.\ 2CaO) + [0.5MnSiO_3.$$

The reduction would be according to the following chemical reaction:

$$4ZnS + 1.1PbS + 1.5FeS + 0.3(SiO_2\ Al_2O_3\ FeO\ 2CaO) + 0.5MnSiO_3 + 5.1CaO + 5.1C = 4Zn + 1.1Pb + 5.1CaS + 1.4SiO_2 + 0.3Al_2O_3 + 1.8FeO + 0.6CaO + 0.5MnO + 5.1CO.$$

To one ton of mineral this requires 285.6 kg. lime, 61.2 kg. of carbon, and forms 261.6 kilograms of zinc, 227.7 kg. of lead, 698.3 kg. of slag, and 142.8 kg. of carbon monoxide.

The total heat necessary for the reaction, calculated as in the preceding case, is 665,000 calories per ton of mineral treated, or 2,560,000 calories per ton of zinc obtained. This in a furnace of 65 per cent. efficiency and with a loss of zinc amounting to 5 per cent. of that in the ore treated, represents an expenditure of 4,800 kilowatt-hours. This figure may appear high, but it should be observed that at the same time that one ton of zinc is obtained, 875 kilograms of lead along with the silver are saved.

The final obtaining of these two metals in a pure state, of course, requires supplementary operations.

Process Involving Separation and Reduction.

For mixed ores, the method of operation may be advantageously modified to utilize the volatility of the sulphides of lead and zinc. The sulphide of lead volatilizes at about 1000°. In the presence of carbon, the sulphide of zinc also volatilizes at about the same temperature. Under the same conditions, the sulphide of iron remains fixed and unaltered. The method of treatment may consist of the following steps:

(1) Separation of the sulphides of lead and zinc.

(2) Reduction of the sulphides of lead and zinc.

The first operation may be effected in a Gin circulating induction furnace in which the two working channels are connected with the two condensers.

The ore is mixed with carbon in excess of that required by the following reaction:

$$2ZnS + C \leftrightarrows 2Zn + CS_2.$$

The mixture of lead sulphide, metallic zinc and sulphide of carbon is led into the condensing chambers, where the reverse

reaction to the above occurs, the zinc is resulphurized, and carbon black forms. The mixture of sulphides is collected, lime and carbon are added, and the whole is heated in a similar furnace for the reduction and condensation of the zinc, as previously described. The slag obtained is simple sulphide of calcium. When the reduction is completed in one channel, the zinc is tapped out, the working door opened, and air is admitted, oxidizing superficially the sulphide of calcium to sulphate, increasing its fusibility, and the liquid slag may be easily run out.

The sulphide of silver is volatilized with the other sulphides, except a quite small quantity which is dissolved by the bath of cast iron, and from which it may be regained by treatment of the iron with lead when the iron is sufficiently saturated.

The method of operation may be still further modified by burning the vapors of the sulphides as they issue from the furnace, and thus forming sulphates and oxides of lead and zinc, which react one upon the other in such a manner as to produce, in the condenser, part of the lead in the metallic state containing all the silver, and a mixture of sulphides and oxides of lead and zinc with some basic sulphate of zinc. The oxidized compounds of lead and zinc thus obtained may be taken to the reducing furnace, mixed with lime and carbon, and then reduced.

This oxidation of the products coming from the furnace reduces slightly the energy requirements, and the lime required in the subsequent reduction by some 50 per cent.

Cost of Producing a Ton of Zinc.

To calculate the cost of a ton of zinc by the Gin process, we will determine the different elements for a given output. We will choose, for example, a works having ten electric furnaces of 1,000 horse-power each and hydraulically driven.

We will imagine the details of a plant which does not exist, but which could be doubtlessly built and operated for the sum mentioned, and even for a less sum in a great number of cases.

The electric power required being 7,600 kilowatts, the works could treat and produce the following tonnages per year of 7,200 hours effective work:

Nature of ore	Tons of ore treated.	Tons of zinc produced.
Calamine, 50 per cent. Zn, calcined	28,000	13,300
Rich blende, 52 per cent. Zn	24,000	12,000
Complex ore from Broken Hill	40,000	9,900

On this basis we can find out for each kind of ore treated the annual expenses, and thus have a basis of comparison, it being understood that the prices of the ore, raw materials, labor, etc., are not absolute and cannot be fixed for any place.

Plan for a Works Using Water-power and Having Ten Electric Furnaces of 1,000 Horse-power Each.

I—Plans	$ 3,000
II—Cost and development of water-power	476,000
III—Construction	76,000
IV—Hydraulic machinery	84,000
V—Electric generators	90,000
VI—Electric motors	5,000
VII—Switchboards	5,000
VIII—Erection	10,000
IX—Electric conductors	16,000
X—Electric furnaces and accessories	100,000
XI—Air and water-cooling plant	800
XII—Casting plant	3,000
XIII—Lining of the furnaces	3,200
XIV—Cranes and hoists	4,800
XV—Inside material-handling machinery	44,000
XVI—Laboratory	1,600
XVII—Repair shop	3,000
XVIII—Ore-handling machinery	10,000
XIX—Electric lighting	600
XX—Portable tools	800
XXI—Cost of transporting and storing material	12,000
XXII—General construction costs	12,000
XXIII—Unforeseen	40,800
Total	$960,000

Cost of Treatment of 28,000 Tons of Calcined Calamine per Year, 50 per cent. Zinc Content, 5 per cent. Loss of Metal, and Producing 13,300 tons of Zinc.

Annual Expenses.

I—Cost of administration and general expenses	$ 20,000
II—Superintendent and assistants	8,000
III—Labor	36,000

IV—Raw materials					
Ore,	28,000 tons	@	$33.20	$933,200	
Carbon,	3,600 tons	@	5.60	20,160	
Lime,	3,100 tons	@	4.00	12,400	
Refractory material,	800 tons	@	8.00	6,400	
Miscellaneous				5,840	
					980,000
V—Maintenance and repairs					30,000
VI—Sinking fund					60,000
VII—Miscellaneous and unforeseen					38,000
Total					$1,172,000
Cost of treatment of a ton of zinc				$17.80	
Total cost, ore included				88.00	

Annual Receipts.

13,000 tons of zinc @ $120	$1,760,000
Excess of receipts over expenditures	$388,000

Treatment of 30,600 Tons of Calcined Calamine by the Present Process, and Producing 13,300 Tons of Zinc Annually.

Annual Expenses.

I—Cost of administration and general costs					$ 20,000
II—Superintendent and assistants					8,000
III—Raw materials					
Ore,	30,600 tons	@	$33.20	$1,022,040	
Fuel,	45,000 tons	@	3.00	135,000	
Carbon for reduction,	18,000 tons	@	1.50	20,000	
Retorts,	40,000	@	.50	20,000	
Condensers,	135,000	@	.04	5,400	
Refractory material,	1,000 tons	@	7.00	7,000	
Miscellaneous				5,560	
					1,222,000
IV—Labor					56,000
V—Maintenance and repairs					30,000
VI—Sinking fund					60,000
VII—Miscellaneous and unforeseen					20,000
Total					$1,416,000
Cost of treatment per ton of zinc				$ 29.60	
Cost of treatment, ore included				106.40	

Annual Receipts.

13,000 tons of zinc @ $120	$1,560,000
Excess of receipts over expenditures	$140,000

Economic Comparison to the Two Processes.

The profits of the electric reduction plant would exceed those of the present-day plant by $244,000—that is, would be nearly double.

Works Producing 12,000 Tons of Zinc, by the Gin Process, from 24,000 Tons of Rich Blende Carrying 52 per cent. Zinc.

Annual Expenses.

I—Cost of administration and general costs				$ 20,000
II—Superintendent and assistants				8,000
III—Raw materials				
Ore,	24,000 tons @ $30.00	$720,000		
Carbon,	3,100 tons @ 5.60	17,360		
Lime,	15,000 tons @ 4.00	60,000		
Refractory materials,	800 tons @ 8.00	6,400		
Diverse,		6,240		
			810,000	
V—Maintenance and repairs				30,000
VI—Sinking fund				60,000
VII—Miscellaneous and unforeseen				40,000
Total				$1,002,000
Cost of treatment per ton of zinc		$23.50		
Cost of treatment, ore included		83.50		

Annual Receipts.

12,000 tons of zinc @ $120	$1,440,000
Excess of receipts over expenditures	$438,000

Works Producing 12,000 Tons of Zinc by the Present Process from 26,500 Tons of Blende Carrying 52 per cent. Zinc.

Annual Expenses.

I—Cost of administration and general expenses				$ 20,000
II—Superintendent and assistants				8,000
III—Raw materials				
Ore,	26,500 tons @ $30.00	$795,000		
Fuel,	40,000 tons @ 3.00	120,000		
Carbon for reduction,	15,600 tons @ 1.50	25,400		
Retorts,	30,000 @ .50	15,000		
Condensers,	110,000 @ .04	4,400		
Refractory materials,	1,000 tons @ 7.00	7,000		
Miscellaneous		5,200		
			970,000	
IV—Ore dressing, 26,500 tons @ $1.75				42,400
V—Labor (dressing not included)				57,600
VI—Maintenance and repairs				30,000
VII—Sinking fund				60,000
VIII—Miscellaneous and unforeseen				20,000
Total				$1,208,000
Cost of treatment per ton of zinc		$ 34.50		
Cost of treatment, ore included		100.60		

Annual Receipts.

12,000 tons of zinc @ $120	$1,440,000
Excess of receipts over expenditures	$232,000

Economic Comparison of the Two Processes.

The excess of profits with the electric furnace would be $206,000, the total profits being almost double those of the present processes.

Works Treating Annually by the Gin Process 40,000 Tons of Mixed Ore, 26 per cent. Zinc and 22.75 per cent. Lead, and Producing 9,900 Tons of Zinc and 8,650 Tons of Lead.

Annual Expenses.

I—Cost of administration and general expenses			$ 20,000
II—Superintendent and assistants			8,000
III—Labor			44,000
IV—Raw materials			
Ore,	40,000 tons @ $30.00	$1,200,000	
[Not including silver content]			
Carbon,	3,000 tons @ 5.60	16,800	
Lime,	11,400 tons @ 5.00	45,600	
Refractory material,	1,200 tons @ 8.00	9,600	
Miscellaneous		6,000	
			1,278,000
V—Maintenance and repairs			32,000
VI—Sinking fund			60,000
VII—Miscellaneous and unforeseen			51,000
Total			$1,493,000

Annual Receipts.

Zinc, 9,900 tons @ $120	$1,188,000	
Lead, 8,650 tons @ $100	865,000	
		$2,053,000
Excess of receipts over expenses		$560,000

A comparison of this last process with that of the ordinary practice would be very complicated, and we may confine ourselves to a simple presentation of the above results.

CONCLUSION.

The electric furnace processes are clearly superior to present methods. They require less expense for labor and distilling apparatus, the operation is continuous, and the losses are very notably reduced. They permit the direct reduction of sulphide ores, and the treatment of complex ores.

It may be stated, with all certainty, that such countries as Sweden, in which are united in the same region considerable

quantities of complex ores with powerful waterfalls, are just suited for the adoption of electrothermic methods.

The case is similar with the famous ores of Broken Hill, in New South Wales, which may be treated by utilizing the waterfalls of the Blue Mountains or of the Liverpool Chain. They might also be treated in New Zealand, where there are powerful waterfalls.

The importance of this electrothermic application is emphasized by the fact that there are at Broken Hill, besides the rich ores, nearly 500,000 tons of tailings, containing 100,000 kilograms of silver, 26,000 tons of lead, and 90,000 tons of zinc.

Similarly, the ores of Tunis, Greece and Sardinia can be advantageously treated by the use of the large water-power available in the French and Italian Alps.

These examples are not the only ones which could be adduced but they suffice to prove the immense interest attaching to the subject, and the unquestionably great value of successful electrothermal processes for treating such ores.

Paris, September, 1907.

DISCUSSION.

Prof. Jos. W. Richards: This paper of Mr. Gin is on the "Electrometallurgy of Zinc," and is a proposition to smelt certain ores, either the oxide of zinc mixed with carbon, or the sulphide of zinc mixed with carbon and lime in the electric furnace, this being of the induction type and a heating agent, the resistor, being melted iron in the trough of the furnace. Sketches of the furnace are shown on page 122. It shows the resistor not to be in a circular shape, but in a rectangular shape. The drawing is not as clear as it might be. It is simply that the resistor has a plan of a rectangular shape. One part of the trough is deep and one part shallow, the idea being there is alternately a deep and shallow part of this circle of iron, so that as Mr. Gin says, there will be some circulation caused by the difference of temperature of the heavy and light parts, and that difference of temperature will cause a circulation of the metal again in the secondary trough. Mr. Gin calculates the energy required to reduce zinc

oxide with carbon, assuming a thermal efficiency of 65 per cent., calculating how many kilowatt-hours will be required per ton of zinc obtained.

Finally he calculates the cost of a large plant containing ten electric furnaces of 1,000 horse-power each for the commercial production of zinc on this plan. His conclusion is the electric furnace process as operated in this way should be clearly superior to the present methods in point of cost, and that a large plant should with reasonable cost be able to make or reduce the zinc at probably double the profit made by the present process.

Mr. Carl Hering: It is a very dangerous thing in a furnace of that kind to contract the cross section of the trough at one place when large current densities or high temperature are used, because it is very likely to cause a rupture of circuit, as I explained in a recent paper before this Society.

Mr. W. McA. Johnson: I have tried a great many things in the development of my process for treating zinc ores. So at one time I thought of using the induction furnace for the electric smelting of zinc ores, the purpose being to save the wear and tear on electrodes. But, as it is necessary to have for zinc reduction a highly reducing atmosphere, the wear and tear on the carbons, even if home-made of crushed coke and tar, is not excessive. Mr. Snyder is attempting to use a Siemens furnace in British Columbia, passing the current and smelting it to a slag and metal. It would be even possible to reduce this wear and tear on electrodes still further by feeding carbon around the electrode, as Mr. Taylor does in his carbon bisulfide furnace.

I can see little or no advantage of the induction furnace for zinc ores, for its cost is large and the saving in expense for electrodes is in the light of my experience negligible.

One thing that struck me in looking over his plans is the fact that he is treating a low grade of ore. Hence, the amount of heat he wastes in sensible heat of slag is enormous. I use a preheater to avoid this, and my furnace is also adapted for higher grade ore. Consequently my heat balance sheet, with preheater of proper design, shows that a 1,000 kw. plant will produce 10,000 tons of spelter.

This is in line with present American concentration practice. I have traveled extensively in the West during the past two or

three years and have seen a great many concentrating mills of the present types. At present, the endeavor is to produce a high-grade zinc concentrate. The successful electric furnace will, in my opinion, be the one that will treat a high-grade zinc product, for the reason that capital cost per ton of product is reduced to a minimum. This is a commercial principle and the endeavor of an inventor, if he wishes to succeed, should be to design his process on broad commercial lines.

PROF. RICHARDS: I would like to say that Mr. Gin has taken low grade ores, because they are evidently representative of the majority of the ores in Europe. In the calculation of the heat in the products, however, Mr. Gin has assumed the heat of vaporization of the zinc which has not yet been experimentally determined, but he has assumed it to be one-half what I think it ought to be. I once made some careful computations on the basis of Trouton's rule, and made it some 25,000 Calories per atomic weight of zinc. The calculation can be found in my "Metallurgical Calculations," Part I.

MR. W. MCA. JOHNSON: I can substantiate Prof. Richards' figure, for I have checked it up by using the variation of vapor pressure of zinc with the temperature as the basis of a physico-chemical calculation, and arrived at substantially the same figure for the latent heat of vaporization: 425 Calories per kilogram of zinc, at the boiling, 920°C.

MR. F. T. SNYDER: As it is evident that Mr. Gin has taken a good deal of trouble in preparing this paper, it is of interest to compare his theoretical figures of electricity consumed with the practical results of continuous operation. Mr. Gin's figures, reduced to tabular form, are as follows:

	Calculated by Mr. Gin. Kilowatt-Hours Required.	
	Per Ton Ore.	Per Ton Zinc.
Pure zinc oxide—80 per cent. zinc	1975	2472
Calcined calamine—50 per cent. zinc	1780	3560
52 per cent. blende	1900	3960
Broken Hill—26 per cent. zinc	1250	4800

Mr. Gin states his results "per ton of zinc." It is more convenient in operating to state the cost results "per ton of ore," as operating smelter costs are proportionate to the tons of ore handled and are practically independent of the metal contents of

the ore. It costs for labor and supplies and general expenses substantially the same to smelt a ton of 26 per cent. of zinc ore electrically as it does a ton of 50 per cent. ore.

The consumption of electricity per ton of raw ore in the electric zinc furnace of the Canada Zinc Company at Vancouver, B. C. over a period of eight months, handling a variety of ore, approximated closely to the empirical formula:

Kilowatt-hours per ton of raw ore $= 650 + 5$ times the per cent of zinc present.

Applying this formula to the grades used in this paper of Mr. Gin, shows the consumption of electricity that can be realized in practice as follows:

	Vancouver Results. Kilowatt-Hours Required.	
	Per Ton Ore.	Per Ton Zinc.
Pure zinc oxide—80 per cent. zinc	1050	1315
Calcined calamine—50 per cent. zinc	900	1800
Blende—52 per cent. zinc	910	1750
Broken Hill—26 per cent. zinc	780	3000

In checking results of electric current consumption, it is to be noted that each pound of zinc per ton of raw ore reduces the amount of slag in the furnace product by two pounds per ton of raw ore.

A paper read in abstract by Dr. Jos. W. Richards at the Twelfth General Meeting of the American Electrochemical Society at New York City, October 18, 1907; President C. F. Burgess in the chair.

THE METALS IN ORDER OF THEIR BOILING POINTS, AS ARRANGED FROM MOISSAN'S EXPERIMENTS IN THE DISTILLATION OF METALS AND ALLOYS.

By Oliver P. Watts.

The widespread introduction of the pyrometer into both scientific and technical metallurgy has resulted in an increase in the accuracy and extent of our knowledge of the melting points of the metals. Their boiling points, however, are still an almost unknown quantity. A knowledge of the latter is of importance to the experimenter with the electric furnace, for in the production of metals from their ores, the boiling point of the metal fixes the maximum temperature of the furnace, consistent with a good yield.

Although it would be most satisfactory to have the boiling points of the metals expressed in degrees centigrade (or Fahrenheit), it is not necessary that they be so stated in order to be of service in electric furnace work. An arrangement in order of their boiling points, with some indication of the magnitude of the intervals between successive members of the series, would be of practical use.

Before the advent of the electric furnace the boiling of metals was an unusual phenomenon, except in the case of the more volatile ones, such as mercury, sodium, potassium, and zinc. In 1893, Moissan[1] established that aluminum, copper, gold, iron, manganese, platinum, silicon, silver, tin and uranium can be distilled in the electric furnace. Twelve years later he returned to this subject, and in a series of quantitative experiments determined the weights of various metals boiled away under the same conditions, and also the changes in composition produced in several alloys by heating them in the electric furnace.

[1] Comptes Rendus, **116**, 1429.

The first experiments consisted of the distillation of alloys of copper with zinc, with cadmium, with lead, and with tin, and of an alloy of lead with tin.[2]

The tube furnace[3] used consisted of a carbon tube passing transversely through the walls and cavity of a furnace consisting of two hollow blocks of lime. The tube was heated by an arc beneath it, and the alloy was contained in a carbon boat inside the tube. The arc furnace also used was made from two blocks of lime, and the alloy was held in a carbon crucible below the arc. The time was reckoned from the melting of the alloy.

I. "Charges of 40 grams of alloy containing 60 per cent. copper and 40 per cent. zinc were heated in the tube furnace by a current of 450 amperes at 110 volts, for periods of 1, 2½, 5 and 8 minutes. In each case the residue was free from zinc."

II. "Seventy-five grams of copper and 25 grams of cadmium were heated in the arc furnace by 400 amperes at 110 volts. Samples of 8 grams, removed at the end of three minutes, and 45 grams, removed after six minutes, contained but a trace of cadmium."

III. Copper and lead.

"*a.* Eighty grams of copper and 20 grams of lead were heated in the arc furnace by 500 amperes at 110 volts. A sample of 20 grams removed after two minutes contained 14.7 per cent. lead, a sample of 30 grams at the end of five minutes contained 5.2 per cent., and 8 grams, after eight minutes, contained only 0.8 per cent. lead."

"*b.* Seventy-five grams of copper and 75 grams of lead, after three minutes' heating by 600 amperes at 110 volts, contained no lead."

"*c.* Ninety-seven grams of copper and 60 grams of lead, heated in the arc furnace for six minutes, left a residue of 45 grams, containing no lead."

"*d.* Charges of 60 grams copper and 40 grams lead were heated in different crucibles, with the following results:

[2] Moissan and O'Farrelley. Sur la distillation d'un mélange de deux metaux. Comptes Rendus, **138**, 1659-1664 (1904).

[3] Comptes Rendus, **117**, 679 (1893).

No.	Total time	Time of distillation	Residue	Per cent. lead
1	4 min.	¾ min.	78 grams	26.6
2	3½ "	1½ "	67.5 "	13.1
3	3 "	1 "	64.5 "	13.9
4	———	2 "	60.5 "	9.1
5	———	2 "	14 "	0.0

"The alloy used in No. 4 was the residue of No. 3, and that used in No. 5 was the residue of No. 4."

IV. Copper and tin.

"*a.* Forty grams of an alloy containing 48 per cent. tin was boiled for one minute in a tube furnace. The residue contained 52.8 per cent. tin, 47 per cent. copper."

"*b.* Charges of 30 grams of an alloy containing 25 per cent. tin were heated in a tube furnace—

No. 1. Two trials, heating 20 minutes, left a residue containing 46.7 per cent. tin.

No. 2. After treating five minutes at 600 amperes, the residue contained 30.5 per cent. tin.

No. 3. Heating ten minutes at 600 amperes left a residue containing 30 per cent. tin."

"*c.* One hundred and forty grams of copper and 60 grams of tin were heated in the arc furnace at 500 amperes. Samples removed at the end of three, six and nine minutes had the following composition:

After 3 minutes, 29.9 per cent. tin.
After 6 minutes, 29.7 per cent. tin.
After 9 minutes, 33.7 per cent. tin."

"c_2. Thirty grams of copper and 70 grams of tin were heated by 500 amperes at 110 volts in a small carbon crucible in a large arc furnace, in order to moderate the action of the arc. The residue contained, after three minutes, 69.4 per cent. tin; after six minutes, 69.5; after nine minutes, 65.5; and after twelve minutes, 62.3 per cent. tin."

"*d.* Thirty-one grams of copper and 40 grams of tin were heated in a small arc furnace by 500 amperes at 110 volts. After

boiling for three minutes, a sample of 16 grams was removed and found to contain 60.1 per cent. tin. After six minutes, a sample of 20 grams contained 59.7 per cent. tin, and after nine minutes, a sample of 9 grams contained 60.4 per cent. tin. This sample of alloy distils in the same proportion as its components."

"c_1. Sixty grams of copper and 40 grams of tin were heated in a covered crucible by 400 amperes at 70 volts. Samples were withdrawn from time to time and analyzed."

	Time heated	Time distilled	Residue	Per cent. tin
1st Exp.	4 min.	2 min.	96.5 grams	40.4
	5 "	2½ "	95 "	—
	5 "	2½ "	85.4 "	41.8
2d Exp.	5 "	2½ "	89 "	40.4
	5½ "	3 "	71.5 "	43.2
	4½ "	2½ "	44 "	46.1
	5 "	— "	31.5 "	50.6

"e_2. Twenty grams of copper and 40 grams of tin were heated by 400 amperes at 70 volts as above, with the following results:

Time heated	Time distilled	Residue	Per cent. tin
4 min.	2 min.	92 grams	79.9
7½ "	5 "	82 "	78.2
6½ "	3 "	62.5 "	77.7
4½ "	– "	51.5 "	76.3

"e_3. Thirty grams of copper and 70 grams of tin, after three minutes' boiling by the same energy as above, left a residue of 65 grams, which contained 65.3 per cent. tin."

V. Tin and lead.

"a_1. Fifty grams of tin and 50 grams of lead were heated in the arc furnace by 400 amperes at 110 volts. A sample of 8 grams removed after two minutes contained 4.8 per cent. lead, and a sample of 20 grams removed after five minutes contained 1.5 per cent. lead."

"a_2. Fifty-five grams of tin and 5 grams of lead, similarly

heated, contained after one minute of boiling 5.8 per cent., and after five minutes, 0.28 per cent. lead."

"*b.* Sixty grams of tin and 40 grams of lead heated in the arc furnace by 450 amperes gave the following results:

Time heated	Time distilled	Residue	Per cent. tin
1½ min.	½ min.	61.5 grams	83.1
2 "	¾ "	59.5 "	87.8
3 "	1½ "	50 "	96.6
2½ "	1¼ "	41 "	99.7

"In the copper-tin mixtures, with excess of copper the tin increases in the residue, but with excess of tin in the original, the tin diminishes in the residue, in each case approaching the composition indicated by the formula CuSn for the residue."

Initial per cent. tin	Time heated	Per cent. tin in residue
25	20 min.	47
40	10 "	50.6
55	5 "	56.8
80	10 "	76.3
70	12 "	62.3
60.2	9 "	60.4

"These experiments show that the boiling point of tin is above that of copper. Since the melting point of tin is 226° C., and that of copper 1056° C., tin shows a very extended range of temperature for the liquid state.

The distillation of metals shows examples of three types of the distillation of liquids:

Copper-lead acts like partially miscible liquids, such as ether and water.

Tin-lead acts like completely miscible liquids, such as alcohol and water.

Copper-tin acts like water and formic acid, having a certain temperature at which their vapor pressures are equal."

The writer would call attention to the fact that the formula CuSn requires 65.1 per cent. tin, instead of 60.4 as obtained by Moissan as a residue of distillation. This divergence may perhaps be due to the carbon with which the alloy quickly becomes saturated. Recent experiments by the writer seem to indicate

that tin dissolves less carbon than copper when heated to very high temperatures. A greater affinity of carbon for copper than for tin would tend to prevent the evaporation of copper, and so might produce the divergence noted above.

Alloys of gold with copper and with tin were next investigated.[4]

VI. Gold and copper.

"Alloys of gold and copper were made containing 10 and 50 per cent. of gold. These were heated with the following results:

Per cent. gold	Wt. taken	Amp.	Volts	Time	Furnace	Residue			Gr. distilled	
						Wt.	Per cent. Cu.	Per cent Au.	Cu.	Au.
10	100 gr.	500	70	4 m.	arc	77	89.02	11.33	21.45	1 28
10	39 "			5 "	tube		89.09	10.72		
50	46 "				arc	44	49.00	52.22	1.44	0 90
50	28 "			7 "	tube	23	42.8	57.02	4.15	0.89

VII. Gold and tin.

Per cent. gold	Wt. taken	Amp.	Volts	Time	Furnace	Residue			Gr. distilled	
						Wt.	Per cent Sn.	Per cent. Au.	Sn.	Au.
40	200	500	70	3	arc	185	59.7	41.8	9.55	2.67
40	200	500	70	4	arc	149	53.88	45.9	39.72	11.61

"In the distillation of the alloys of gold and tin the furnace contained a copper tube cooled by a stream of water, and a bell glass was placed over a hole in the top of the furnace. The purple of Cassius condensed in the bell glass, having the composition 49.15 per cent. SnO_2, 36.93 per cent. CaO, 9.90 per cent. gold. The lime was removed by treatment with dilute hydrochloric acid to obtain the pure purple. Other oxides act similarly when vaporized with gold. Alumina yields a pale rose color, magnesia a violet, zirconia a rose or violet, and silica a fine purple color."

The last alloys to be tried were those of silver.[5]

"These experiments were carried out in a graphite boat in the tube furnace described in Comptes Rendus, *138*, 1659 (1904). The metals were especially prepared for this research. The

[4] Moissan. Sur la distillation de l'or, des alliages d'or et de cuivre, d'or et d'etain, et sur une nouvelle préparation du pourpre de cassius. Comptes Rendus, **141**, 977-983 (1905).

[5] Moissan and T. Watawabe. Sur la distillation des alliages d'argent et de cuivre, d'argent et d'etain, d'argent et de plomb. Comptes Rendus, **144**, 16-19 (1907).

alloys were made and analyzed, the residue was analyzed after each distillation, and the distillate was found by loss. Time was reckoned from the moment the alloy became liquid. The current was kept as constant as possible at 500 amperes and the voltage at 110. Vaporization began in 35 seconds, and after three minutes a certain amount of graphite had been dissolved by the alloy."

VIII. Silver and copper.

Time. Minutes.	Weight Taken.	Residue.	Loss.	Loss per cent.	Composition of alloy.				Grams distil'd.	
					Initial.		Final.			
					Silver.	Copper	Silver.	Copper	Silver.	Copper
1	39.1434	38.2113	0.9321	3.	48.85	51.04	49 86	50.64	0.070	0.630
2	39.7698	38.9113	0.8585	2.16	"	"	49.29	50.89	0.248	0.496
3	40.5854	36.1218	4.4636	11.	"	"	45.11	54.63	3.531	0.982
4	40.0604	35.6215	4.4389	11.08	49.12	51.18	47.42	52.02	2.782	1.973
5	40.5914	22.0588	18.5356	36.28	"	"	20.91	78.64	15.322	0
6	40.3194	20.8413	19.4781	48.31	"	"	17.98	81.34	16.052	3.630
7	36.1314	21.6544	15.4770	42.84	"	"	18.54	81.27	13.729	0 893
9	38 9549	26.4700	12.4849	30.60	49 55	49.65	18 33	80 70		
13	39.5539	13.6100	25.9439	65.59	"	"	4 77	94.43	18.404	6.786
15	39.3404	6.7740	32 5664	82.77	"	"	3.62	95.22	19.249	13.111

"During the first three minutes there is little change in the amount of silver in the boat, and the amount of vapor may be regarded as nearly constant to the sixth (fifth?) minute. Then the amount of silver in the alloy suddenly diminishes. It is possible that up to the beginning of the fourth minute there was a definite alloy, but this would be stable only in the liquid state, for a metallographic and physical study of the alloys of copper and silver does not indicate the existence of any definite compound of these two metals. The longer the distillation, the richer the alloy in copper. The boiling point of copper is then higher than that of silver."

The weights of each metal distilled were not given in Moissan's tables, but have been computed and added by the writer. There is some error in the data given for the distillation of nine minutes duration, for, according to the composition stated, the original alloy contained 19.302 grams of silver and 19.341 grams of copper, and the residue contained 4.850 grams of silver and 21.361 grams of copper, so that the amount of silver distilled would be about 2 grams more than the total loss in weight, while the copper

shows a gain in weight of nearly the same amount as a result of the distillation.

IX. Silver and tin.

"Moissan and O'Farrelley have established that the boiling point of tin is higher than that of copper. It was of interest to see if there was a decided difference between the boiling points of tin and silver. The alloy was heated under the same conditions as for the alloys of silver and copper, and vaporization began ten seconds after fusion. Silver, like copper, has a lower boiling point than tin."

Time Minutes.	Weight of Alloy.	Weight of Residue.	Loss Grams.	Loss Per Cent.	Composition of Alloy.				Grams Distilled.	
					Initial.		Final.			
					Silver.	Tin.	Silver.	Tin.	Silver.	Tin.
2	40 7328	39.6966	1.0362	2.55	36.98	64.04	33.72	65.53	1.678	0.0655
6	40.7481	17.8956	22.8525	56.08	"	"	10.14	88.87	13.2544	10.1910
10	39.0705	9.4836	29.5869	75.73	"	"	2.83	93.65	14.1798	16.1367

X. Silver and lead.

Time Minutes.	Weight of Alloy.	Weight of Residue.	Loss Grams.	Loss Per Cent.	Composition of Alloy.				Grams Distilled.
					Initial		Final.		
					Silver.	Lead.	Silver.	Lead	Silver.
1	40.9330	28 6775	12.2955	30.04	46.24	52.95	60.75		1.5045
2	38 7852	3.1460	25.6392	66.10	"	"	83.06		7.0110
2½	42.8045	4.3244	38.4801	89.89	"	"	96.81		15.6078

Experiments in the distillation of copper[6] and of the metals of the platinum[7] and iron[8] groups, and of titanium[9], were carried out in the arc furnace with a tube of copper of 15 mm. bore placed just above the crucible and 2 cm. from the arc, to serve as a condenser. The tube was cooled by a stream of water forced through it by a pressure of 10 atmospheres. A tall bell glass was set over the hole in the top of the furnace to serve as an additional condenser. These experiments are summarized in the following table:

[6] Moissan. Sur la distillation du cuivre. Comptes Rendus, **141**, 853 (1905).

[7] Moissan. Sur l'ebullition de l'osmium, du ruthenium, du platine, du palladium, de l'iridium, et du rhodium. Comptes Rendus, **142**, 189-195 (1906).

[8] Moissan. Sur l'ebullition du nickel, du fer, du manganèse, du chrome, du molybdène, du tungstène, et de l'uranium. *Ibid.*, pp. 425-430.

[9] Sur la distillation du titane et sur la temperature du soleil. Moissan. *Ibid.*, pp. 673-677. A single article covering all of these experiments may be found in Annales de chimie et de physique, 8, 145-181 (1906).

Metal	Grams taken	Furnace	Min. heated	Energy Amp.	Energy Volts	Grams distil'd	Remarks
Copper	300	arc	5	300 x	110	50	Filaments of copper condensed on the cold tube. The residue is covered by a coating of graphite.
"	"	"	6	"	"	160	
"	"	"	8	"	"	233	
Gold	150	"	5½	500	110	10	Residue is covered by a film of graphite, and is 99.98% gold. Cavities in its outer surface indicate the absorption of gas.
"	"	"	6½	"	"	20	
"	"	tube	4	"	"	17	
Osmium . . .	100	arc	4	500	110		Vapors condensed on cold tube. Meta not melted.
" . . .	"	"	5	600	110	16.5	Only partially fused.
" . . .	150	"	5	700	"	29	Entirely melted. Residue contains 3.9% graphite.
Ruthenium . .	150	"	3	700	"	16.5	Fused and boiled. Residue = 4.8% graphite.
" . .	"	"	5	500	"	10	Boiling point lies between those of Pt and Os.
Platinum . .	150	"	5	500	"	12	Ingots contain blow holes, proving the evolution of gas, and also contain graphite.
" . .	"	"	6½	"	"	19	
Palladium . .	23		2	500	"	3.2	Boiled. Residue saturated by carbon.
" . .	150	arc	5	"	"	9.63	Metal boils quietly and "wets" walls of crucible.
Iridium	150	"	5	500	"	9.0	Metal boils quietly and "wets" walls of crucible.
Rhodium . . .	5	tube	1½	500	"	—	Melted in 30 sec. Vapors condensed.
" . . .	150	arc	4	"	"	4	Melted and boiled.
" . . .	"	"	"	"	"	6.1	Residue = 2.19% carbon.
" . . .	"	"	5	"	"	10.2	Drops and crystals of metal condensed on cold tube.
Nickel	150	"	5	500	"	56	Distillation began in 1 minute. Cold tube is coated by microscopic crystals.
"	200	"	9	"	"	200	
Iron	150	"	5	500	"	14	Distillation of iron is difficult because of violent evolution of gas just below the boiling point.
"	825	"	20	1000	"	400	
Manganese . .	150	"	5	500	"	80	Metal used contained 2% carbon.
Chromium . .	150	"	5	"	"	33	Residue is chromium carbide.
Molybdenum .	150	"	5	500	"	0	Not melted.
" .	"	"	5	700	"	0	Well fused. Evolves gas like iron.
" .	"	"	20	"	"	56	Metallic cubes and octahedra on cold tube.
Tungsten . . .	150	"	5	500	"	0	Not melted.
" . . .	"	"	20	800	"	25	Boils at higher temperature than any other member of the iron family.
Uranium . . .	150	"	5	500	"	0	Fused.
" . . .	"	"	5	700	"	15	Residue is a carbide.
" . .	200	"	9	900	"	200	Abundant vapors in 4 minutes.
Titanium . . .	500	"	5	500	"	9	Only the surface was melted.
" . . .	150	"	5	"	"	11	The titanium used contained 3.2% carbon.
" . . .	150	"	6	"	"	17	
" . .	300	"	7	1000 x	55	110	All fragments were melted but the surface was not horizontal.

All of these metals take up carbon when melted. The metals of the platinum group are quickly melted and brought to the boiling point. With 150 grams of metal, fusion occurs in one to two minutes, and boiling in four minutes. The following details concerning the distillation of a few metals, may prove of interest:

Palladium.—"One hundred and fifty grams of metal, at 500 amperes and 110 volts, melts quickly, 'wets' the walls of the crucible, dissolves carbon, and finally boils quietly. Vapors condense on the cold tube and escape around the electrodes. The melted lime, which extends a certain distance from the crucible, is colored black. If 150 grams of palladium, saturated with carbon, be withdrawn from the furnace and allowed to cool, graphite comes to the surface and covers it with lamellar, superimposed crystals. When a solid crust is formed, one hears sharp cracklings, the surface of the metal cracks, and here and there brilliant drops and crystalline mushrooms of melted metal appear. The surface of the metal is of a bluish color, with rainbow reflections, and shows dendrites at right angles and confused crystals. On the cold tube there is a coating of very small crystals mixed with metallic spheres."

Iron—"The distillation of iron presents a new difficulty. As soon as it takes up carbon and is melted, it absorbs a large amount of gas, as many experimenters have proved. A little below its boiling point these gases escape rapidly and throw out drops of metal. This can be proved by placing 50 grams of iron in a boat in the middle of a carbon tube which passes through the electric furnace. On heating the under side of the tube for several minutes, the metal is seen to melt rapidly, preserving a perfectly horizontal surface. After several seconds, the temperature continuing to rise, bubbles of gas begin to break the surface, then there is an abundant shower of drops, and by the end of the third minute, the remaining liquid boils quietly. In stating the weight of iron distilled, allowance was made for this spattering of the iron. After the distillation, a felting of small, brilliant, clear gray crystals is recovered from the cold tube, but these agglomerate if the heating is prolonged. The distilled metal takes the form of the tube. Sometimes one finds in the midst of the distilled product clusters of interlacing scales, apparently welded at the base, and spindle-shaped. There have been found,

too, square shapes, and an octahedron, which seemed to be formed of piled up crystals; but usually these forms are very vague, for the condensation of the vapor is much too rapid to admit of regular crystallization. If the experiment is a little prolonged, the lime distills at the same time the iron is depositing on the tube, then melts and acts on the metal. When the lime which forms the furnace contains sulphates, the distilled metal includes a small quantity of sulphide of iron.

"The crystalline dust obtained in all of these experiments by condensation of the metallic vapor on the cold tube has the same chemical properties as the metal when ground fine."

From the extensive data quoted, obtained by Moissan and his co-workers, the writer has attempted to arrange the entire series of metals treated, in the order of their boiling points. This is a difficult task to accomplish satisfactorily, and probably an impossible one to carry out with complete accuracy. In several cases the difference between the weights of two metals distilled is within the limit of experimental error. The specific heats and unknown latent heats of vaporization may also cause errors in the tabulation, as the writer could not make allowance for these factors. The only known points in the series are the boiling points of zinc, 940° C., and of copper, 2100°., C., as determined by Féry.[10] The boiling point of tungsten was then assumed to be 3700° C., and the other metals were arranged between these limits. The number standing opposite each metal is not claimed to be its boiling point, but only as an indication of its relative position in the series which begins with zinc at 940° C., and ends with tungsten at some unknown temperature above the melting point (3200° C.).

Zinc	940°C	Titanium	2700°C
Cadmium	1025	Rhodium	2750
Lead	1250	Ruthenium	2780
Silver	1850	Gold	2800
Copper	2100	Palladium	2820
Tin	2170	Iridium	2850
Manganese	2200	Osmium	2950
Nickel	2450	Uranium	3100
Chromium	2500	Molybdenum	3350
Iron	2600	Tungsten	3700
Platinum	2650		

[10] Annales de chimie et de physique [7], 18, 428 (1903).

The order for the first six metals with reference to each other is correct, since it was obtained from the distillation of alloys. The position of manganese with reference to tin and copper is doubtful. Gold is surprisingly high in the series, and if correctly placed, is second only to tin in the wide range of temperature of its liquid state. Further and more conclusive experiments may lower the position of gold. Moissan's experiments show that there is considerable vaporization of titanium before it melts, but even so, the low position here necessarily assigned for its boiling point must be a surprise to anyone who has tried to fuse this extremely refractory metal. The writer thinks that further experiments, particularly in the absence of air, may greatly change the place of titanium.

With the greatly regretted death of Moissan, this series of experiments has been brought to an untimely close. Now that he has established that the most refractory metals can be distilled with ease and regularity in the electric furnace, it remains for others, with the aid of the optical pyrometer, to ascertain the exact boiling points of the metals, and so fill a wide gap in our knowledge of the constants of Nature.

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DISCUSSION.

Prof. Jos. W. Richards: This is a discussion of Moissan's experiments in the distillation of metals and alloys in the electric furnace. The alloys taken are copper and zinc, copper and cadmium, copper and lead, copper and tin, tin and lead, gold and copper, gold and tin, silver and copper, silver and tin, and silver and lead, and then some experiments on the metals themselves, copper, gold, osmium, ruthenium, platinum, iridium, rhodium, nickel, iron, manganese, chromium, molybdenum, tungsten, uranium and titanium, to determine the ease with which they volatilized in the electric furnace.

Having gathered that information together from a great many different publications of Moissan, Dr. Watts has drawn some conclusions, or tried to, as to the relative volatility of these differ-

ent metals, and on page 151 he has drawn up a statement in which he shows the boiling point of zinc at 940°C.; the boiling point of copper, as determined by Fery, is 2,100°C., and that of tungsten was assumed to be 3,700°C., and the other metals are arranged in that schedule in their relative order as derived from these experiments, and given a provisional temperature, it being clearly stated that the temperature given is only provisional and not absolute, but that the relative position of those is probably correct.

In the way of discussion, I think Dr. Watts has done a useful thing in getting the data together. We must bear in mind, however, that many of these data are determined from alloys, and not by accurate tests on the pure metals, such as zinc, cadmium, lead, silver, copper, tin, manganese, etc., and I think that a radical mistake has been made in drawing conclusions as to the relative volatility of the metals from their relative volatility from alloys, because the volatilizing of a metal from an alloy is like boiling one substance from another in solution. You cannot draw an exact inference as to the relative volatility or the boiling point from different solutions. As an example of that, I notice by the table that the boiling point of zinc is taken as 940, and that of cadmium is estimated as 1,025. It appears from these experiments that from some alloys cadmium volatilizes more difficultly than zinc. This estimated boiling point, however, is contrary to the facts as to the volatility of cadmium and zinc, since we know that the boiling point of cadmium is 775°, and of zinc 930°.

The evident cause of that discrepancy is that the alloys of cadmium and copper, let us say, are stronger than the alloys of zinc and copper, and in consequence the cadmium is held tighter by the copper and comes off at a relatively higher temperature than the zinc. That source of error permeates all these experiments made on the alloys, and the inferences drawn from them.

Mr. Watts *(Communicated):* I thank Prof. Richards for correcting my error in placing the boiling point of cadmium above that of zinc, and for his very clear explanation of its cause. This source of error applies, however, only to the relative order of cadmium, zinc and lead, not to all the experiments with alloys, as stated by Prof. Richards. The order of the boiling points of lead, silver, copper and tin may be accepted as set-

tled by the experiments described since an alloy or a mixture of each metal with that next in order was boiled, and the weight of each metal distilled was determined. With alloys of silver and copper, experiment VIII, the weight of silver distilled exceeded that of copper, hence silver has the lower boiling point. Similarly for the alloy of silver and lead, lead proved to be the more volatile, and of copper and tin, copper was slightly more volatile.

A paper read at the Twelfth General Meet- of the American Electrochemical So- Society in New York City, October 18, 1907; President C. F. Burgess in the chair.

A NEW APPLICATION OF CHLORINE IN METALLURGY.

By Chas. E. Baker.

The term refractory, applied to ores, is generally understood to cover such as have the valuable metals, combined or associated with such elements as sulphur, arsenic, antimony, selenium, or tellurium. Inasmuch as most of them are sulphides, this paper will deal with the manner of treating sulphide ores.

The usual method is to use the sulphur as a fuel, as in pyritic smelting, or by its combustion in roasting to oxidize it; either of these processes destroys it. When ore is roasted, moreover, the surrounding atmosphere is polluted by the poisonous gases eliminated. The result is much damage to vegetation, many lawsuits, and, finally, the bringing of legislation against the practice. It has become a serious question, and is likely to be more so when legislators learn that ore can be economically treated without creating this nuisance. The methods for putting gold into solution, either by cyaniding or wet chlorination, require ore that has been oxidized, either by roasting or by the natural action of the elements. In either case, the oxidation is imperfect, and the extraction of the gold only partial.

The discovery of the cyanide process was the greatest improvement in gold extraction that has taken place in a century. The key to this cyanide process is in the production of the gold solution. If the metallic contents of any ore can be changed so as to make them soluble, the recovery of the metal is then easy. These processes for handling gold will not apply to base metal extraction. The most plentiful and cheapest element that will produce base metal solutions is chlorine. Found in common salt, it is available almost everywhere. Improvements in electrical devices and in the knowledge of electrolysis have now made the decomposition of salt by electrolysis commercially successful. The cost of chlorine is more than offset by the value of caustic soda, obtained simultaneously with its production. Therefore,

working thus, *chlorine costs nothing*. The process I have been developing for about five years, on which I have spent many thousands of dollars, uses chlorine so obtained, and is intended for the extraction of metals from refractory ores described here as sulphides, although applicable to arsenides, tellurides, etc., with unimportant alterations in the application of the chlorine and mechanical handling. The finely pulverized, practically dry ore is placed in the porcelain-lined mill, commonly known as the tube mill, provided with lead-lined trunnions, and supplied with flint pebbles. It will be referred to hereafter as the drum. We consider this mill to be necessary for the prosecution of the work. We know of no other means for completing decomposition, especially in handling zinc sulphides. The chemical action generates so much heat that the chloride formed becomes melted, or volatilized, and spreading to surrounding particles, covers them over as by a varnish, preventing further action by chlorine. As the drum revolves, the flint pebbles grind the particles, presenting continuously fresh surfaces to be acted on. They also tend to break up or prevent any clodding or balling of the mass. The gas is admitted to the drum, and acts at once on the ore. The metal combines with the chlorine, liberating the sulphur. As the chemical attraction of chlorine for metal is greater than it is for sulphur, sulphur chloride is only formed as the metal contents decrease. The drum revolves during the operation, and chlorination of the metals is effected, leaving sulphur free with the gangue, provided no heat is applied and the supply of chlorine stopped when the metal is chloridized. But if the drum be heated, sulphur chloride is formed, and at about 150° C. is expelled as a gas, and may be condensed. It makes a by-product of much more value than sulphur, being salable at 10 cents per pound. Arrangements can be made to take care of extra and escaping chlorine by having two drums in tandem, or by passing it into a bleach chamber.

The process *proper* ends here. We have the chlorides, and the sulphur has been eliminated from its combination, and made available for revenue. But while the process, so far as the patents extend, has ended with the work of decomposition, it is not *all* of it. The recovery of the chlorine for use again is a necessary part, as is also that of the recovery of the metal. If the process

be illustrated as applied to a lead-zinc sulphide ore, carrying gold and silver, the contents of the drum after chlorination would be emptied into leaching tanks, the soluble chlorides removed, leaving behind in the gangue with the free gold any insoluble silver or lead chlorides remaining. In the presence of plenty of other chlorides they are both partly soluble, and in most cases they will be carried forward with the other solutions. During chlorination, the iron forms ferrous chloride, and gold will not become soluble in its presence, nor when chlorine is dry. The gangue, freed from all base metals and containing the free gold, is in fine condition for gold extraction, much better than if from a roasted ore. It may be recovered by wet chlorination, by cyaniding, or by amalgamation in barrels. It will be too fine for *plate* amalgamation. Silver may be recovered by leaching with sodium hyposulphite. Purification of solution follows. Granulated lead precipitates copper, granulated zinc precipitates lead. The remaining solution would then contain ferrous and zinc chlorides. Chlorine must be supplied to make the iron ferric chloride, then zinc oxide precipitates ferric hydroxid, forming zinc chloride. Electrolysis then produces practically pure zinc, and the chlorine is liberated for use again. Suppose the ore handled be one whose principal ingredient is copper. It chloridizes as cuprous and cupric salt, either or both. If it should be cuprous, it is then only partially soluble. But it is readily soluble in other chlorides, especially of sodium or calcium. Electrolysis then produces copper, liberating chlorine, the iron chloride remaining undecomposed, at the low voltage used in copper electrolysis. No deposit of copper takes place until the cathode department becomes cuprous. In a large plant in Germany where a pyrite cinder is being handled, the chloride solution contains copper, iron and zinc. Copper and zinc are being produced from the same solution on a large scale, each practically pure. Last year's zinc output averaged about 2¼ cents per pound above the market price for spelter, owing to its purity. You are no doubt familiar with the Swinburne-Ashcroft method of handling ores by chlorine under pressure. It produces, by chemical action alone, a temperature of from 600° to 700° C., but is limited in its application to ore carrying not over about 30 per cent. gangue, *i. e.*, to concentrated material. The difference

between their system and this is apparent. Much gangue would block them off mechanically, while we prefer having the gangue to keep down the temperature, to avoid volatilizing the chlorides. In their case sulphur vaporizes. I do not refer to their process for the purpose of criticism. I only wish to call your attention to the differences and to show that the wasteful, expensive system of concentration is neither necessary nor desirable for ours.

The concentration of ore should be only for the purpose of saving transportation expenses, as losses by concentration are very heavy. This subject is worth your attention. Cut out smelting, roasting and concentration, and replace them with chemical and electrochemical methods. Chlorine is the element for the work, either as such or as the active element of hydrochloric acid or other chlorides.

Here is an illustration of an application of chlorine in the form of hydrochloric acid as the chloridizing agent. The silicate of nickel-aluminum-magnesium-iron, forming the garnierite ore found in New Caledonia, presents an almost impossible smelting proposition, as the main ingredient is magnesia. It can readily be handled by hydrochloric acid, and, after chloridizing, the acid is recovered from the base metal chlorides by calcination and used again, the nickel *only* retaining chlorine. We worked this process out to apply on a similar ore, found in North Carolina, and it will also apply to another deposit found in Oregon.

The calcination of the chloridized silicate drives off the hydrochloric acid, and at the same time renders the gangue granular and readily leachable. Here is an application of chemistry to an ore carrying only about 1½ per cent. nickel with 15 to 25 per cent. magnesia. Smelting such would be impossible, yet the expense was light, because the consumption of hydrochloric acid was, in the end, limited almost to the requirement of the nickel for its chloride. From the nickel chloride so formed we produced metallic nickel electrolytically, recovering the chlorine. No smelting at any stage. Other uses will be found for chlorine in metallurgy. By its use it should be possible to build up a by-product industry in the mining business similar in its effect to that of the by-products of the petroleum business. Many of us will remember that illuminating oil furnished the only source of revenue from petroleum at first. Now the by-products are

reported to be the most valuable. Here is a case, indeed, where "the tail wags the dog."

At one time we treated a copper sulphide ore carrying 20 per cent. copper, and recovered bismuth, having a greater value than the copper, even in so rich an ore. Which is then the by-product? Modification of the process will take place, of course. Methods for handling solutions in leaching and purification will be improved on. Some of the pressure or vacuum filter apparatus may be found useful. Some may seek methods for chloridizing which evade our patents, and then will claim originality themselves. We expect that—in fact, we already have such a case. The field is a new one; we have touched only on the main points—much is to be learned. I feel sure that it will pay you to give it your attention. The production of chlorine goes on continuously, first from salt, then from metal chlorides, and this can only be done by electrolysis. The cells to be used for all the work must be so constructed as to save the chlorine, and therefore must be supplied with diaphragms, and have the anode compartment hooded. There are various cells in commercial use, electrolyzing salt, almost any of which may be used, but for metal recovery the cells used should be arranged so that the cathodes will receive the deposit on each side, having one more anode than cathode. The connections are parallel in each vat, the vats connected in series, the sizes made to fit the current used. In handling ore for copper recovery from chloride solutions the voltage is much greater than it is in the refining from soluble anodes in sulphate solutions. Therefore it would at first glance appear to be prohibitive. But the excess energy is partially offset by the double rate of copper deposition. I believe that copper can be produced from ores this way much cheaper than by the old method of concentration, matte smelting, Bessemerizing to blister copper, casting into anodes and sulphate refining by electrolysis, with its subsequent handling of the gold and silver and other electrolytic slimes. All these extra steps are eliminated by this method. The chlorine method would prevent the danger of carrying arsenic and antimony in the copper, because they would not follow into the solution, but would pass out with the sulphur chloride instead. In my opinion, the solution method is preferable to fusion in handling zinc chlorides. They are

easier handled, avoiding the difficulty in drying and fusing. We have obtained solid iron from ferrous solutions. As the general run of ore carries iron, its value as a by-product may be worth considering. My limited means and time prevented extended research work along that line, but I can see no necessity to consider iron as waste. I know no other field for research work so good as this for electrochemists.

It may appear as if I should fill this paper with dry statistics about voltage, amperages, anode and cathode measurements, materials for construction of cells, etc., but I had rather not. My part of the work ends with the production of the chlorides. In commercial practice, it will be found that two kilowatt hours will produce about one pound of chlorine, zinc, iron or nickel, and about 4 pounds of copper or lead. In the case of lead, these figures are derived from the electrolysis of the fused chloride, where some of the energy was used to maintain fusion. If it be doubted that the metals can be recovered commercially from their chlorides, I must call your attention to the successful plants operating in England and Germany producing from such solutions nearly pure nickel, copper and zinc. The English concern has frequently advertised its zinc, 99.98 per cent. pure, in our standard journals. The output of the German concern is in tons daily, copper, zinc and nickel, and such a scale is not a laboratory experiment. It might be proper to name some of the advantages of this method as compared with smelting. Roasting is avoided, with its expensive furnaces and suits for damage from the poisonous gases evolved. Concentration is avoided, with its expensive machinery and power requirement, and with its losses of 15 to 20 per cent. of the values. The sulphur is recoverable for market. Volatilization and slagging losses do not occur. Any refractory ore can be rendered free milling, with the sulphur so thoroughly eliminated that the per cent. of extraction would be very high. In the case of tellurides, tellurium chloride goes into solution and is leached away, leaving the gold free in the clean gangue. No loss there by volatilization. If I were to name here what per cent. extraction we obtained in handling tellurides, you would discredit the statement. When our work is finished, the metals are ready for market, with no need for any subsequent outlay for refining. There being no

reagents necessary except chlorine, the mine owner could handle his own ore independent of anybody, and if he could corral his water-power, he could produce his own electricity at points where coal and coke could not be obtained. In handling zinc-lead sulphides where there is considerable zinc, smelters either refuse downright to take them, or they penalize them for the zinc they contain beyond a given per cent.

This process is especially adapted to such ore. The chemical action is prompt and efficient, the decomposition almost perfect, and there are no volatilization losses. It produces a finished product of the highest grade. In nickel-cobalt ore, the cobalt can be precipitated as a hydroxid from its chloride as a step preceding the nickel electrolysis. Its advantage in handling the cobalt-nickel arsenides of Canada is apparent. At present, mine owners get little beyond a reduced proportion of the silver content, but the arsenic would be saved as a commercial product.

Cleveland, Ohio,
September 7, 1907.

DISCUSSION.

Mr. Carl Hering: It seems to me Mr. Baker passes over lightly what seems to be rather an important part of the proposition, and that is, the cost of the production of the chlorine. He starts out by saying the cost of the chlorine is nothing. It seems to me in following up these reactions, all the high temperature heat which is generated in the process has to come ultimately from the electric current which produces the chlorine. The cost of the chlorine produced by electrolysis, therefore, seems to become a very important item.

Mr. Baker: Whenever chlorine is produced there is a by-product of value obtained. When from salt, caustic soda; when from metallic chlorides, metal. Caustic soda more than pays for the cost of the energy used to produce chlorine. So, therefore, in this case chlorine costs nothing. When chlorine is obtained by the electrolysis of the metallic chlorides the expense should be charged against the metal account. It is a question in bookkeep-

ing. It is proper to charge the cost against the material that produces the revenue. Therefore, in metallic chloride electrolysis the chlorine again costs nothing.

PROF. C. L. SPEYERS: How is Mr. Baker able to regulate the action of the chlorine to prevent the gold from going into solution?

MR. BAKER: In such dry conditions as shown gold does not combine with chlorine. Therefore when the material is placed in water the gold, which is free, does not go into solution because of the presence of ferrous chloride. The ores are treated practically dry, or as they come from the mine. Under these conditions neither gold nor platinum form chlorides. Absolutely dry chlorine does not attack anything.

PROF. SPEYERS: We have here a solid consisting of different substances, touching each other at various points only—not like a solution of several bodies. Consequently the ferrous salt cannot protect the gold from the chlorine. If the ore is so dry that the chlorine cannot act on the gold, I think we should assume, until experiment shows us to be wrong, that the other components are likewise protected from the gas. However, Mr. Baker comes out right in the end—I understand the significance of his remarks now—because he stops the reaction before the ferrous chloride changes to ferric, and consequently in the following lixiviation the gold chloride, which I claim is formed, is reduced to metallic gold, as it was in the beginning in the raw ore. Apparently, but only apparently, the chlorine does not attack the gold.

PROF. RICHARDS: It is undoubtedly true that under these conditions dry chlorine gas will not attack gold. The gold would remain metallic in the residues and not go into solution.

W. MCA. JOHNSON *(Communicated)*: I hesitate to criticise Mr. Baker's paper, for he is a sincere enthusiast, who is game enough to back his opinions with his own money. I believe, however, he is on the wrong track.

His process may show a high recovery; it may even operate at a small labor charge, which is doubtful in view of the small electric melting pots. It may even be operated in a plant at a low cost for repairs, which any chemical engineer will tell you is impossible; but even granting all these good points, which will

in the nature of things be only attained at the cost of many trials, if attained at all, his process has the fatal weakness of an extremely high capital cost per ton of product. This is a vital commercial principle, and especially true in America, where the "density of operation" or tonnage divided by capital cost of plant must be at a maximum. For this reason the "Chlorine Process" will not have any great success, in my opinion.

Another way of expressing the same view is this: The "Chlorine Process" as outlined by Mr. Baker resembles too much the ordinary chemical analysis. A series of operations that deals in milligrams, is not suited for work that is measured in tons. At the Orford Copper Works we used to have about every two months a process put up to us by some enthusiast who would dissolve his iron, nickel, copper, etc., then separate his Group I, Group II, A and B, in the same old way. It was simply quantitative analysis "writ large."

Similarly I would not be afraid of the "Chlorine Process," even with an old retort plant. When times were bad I would run on low grade ore and not lose any money. When times were good I would operate and in one year make as much money as the chlorine process in five years. I could not say this, however, of the electric furnace, as against the old retort plant.

Mr. Baker *(Communicated):* I regret that I fail to impress on Mr. Johnson that we recover the metals from aqueous solutions instead of by fusion. His remarks are directed against the fusion method put forth by Swinburne and Ashcroft. This is shown by his reference to "small melting pots," chemical engi neering problems and large cost of plants.

None of these apply to us. There are no troublesome engineering nor excessively expensive plants—certainly nothing as expensive as for smelting. It is a much cheaper method for metal extraction than any other process that I know of in use to-day, *including electric smelting.*

A paper read at the Twelfth General Meeting of the American Electrochemical Society, in New York City, October 18, 1907; President C. F. Burgess in the chair.

ON THE HEAT CONDUCTIVITY OF CARBON.

By Francis A. J. FitzGerald.

In constructing electric furnaces, one of the most important points to consider in the design is the attainment of the most economical use of the heat energy. The cost per calorie is enormously greater when heat is generated by means of an electric current than when produced by the combustion of fuel; but, fortunately, the utilization of the heat generated is, in general, far more efficient in the case of the former than in that of the latter. We, unfortunately, have no trustworthy data on which to calculate the efficiency of electric furnaces, and therefore it is necessary to devise methods by which we can form an estimate as to the economy with which we ware using our heat.

The problem of making these determinations is not by any means an easy one, but, perhaps, a relatively simple way of studying the matter is to attempt the estimation of the various heat losses. To illustrate this, an example may be taken from an investigation, by no means complete, of a determination of the total heat losses in the case of a small electric furnace. In this experiment, the furnace is used simply for the purpose of raising the temperature of the contents, no chemical reaction being desired. The energy supplied to the furnace is measured and the temperature determined at frequent intervals, until finally a point is reached, or nearly reached, where the temperature remains constant, and consequently all the heat generated is merely supplying the losses, by radiation, conduction, etc. In Fig. 1 is shown a curve illustrating an experiment of this sort. Here a small electric furnace was heated, by means of a resistor, and the temperature determined every six minutes, while the rate of generation of energy was kept constant. The form of the curve shows plainly how rapidly the efficiency of the furnace falls off, until finally the point is nearly reached where the losses balance the generation of heat in the resistor.

It is, however, not sufficient to determine merely the total heat losses in an electric furnace; it is also important to know quantitatively the losses of heat which occur in various ways. Now, some of the most troublesome parts of an electric furnace are the terminals. In general, these terminals are made of carbon, and it appears probable that the heat conducted by these from the charge must form an important item in the heat losses of the furnace. This being so, it is important to obtain some knowledge of the heat conductivity of carbon. In a paper by FitzGerald and Forssell,[1] at the last meeting of the American Electro-

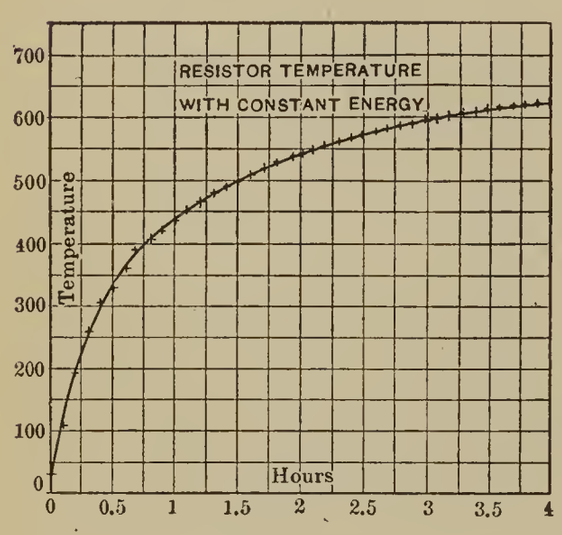

FIG. 1.

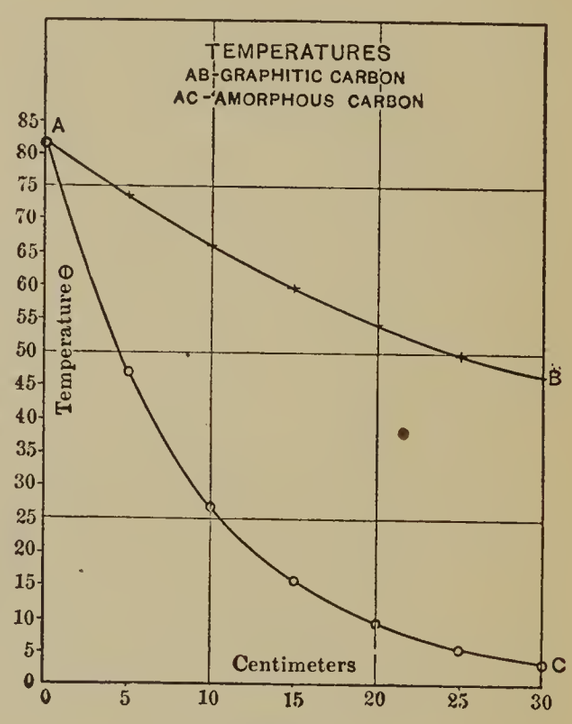

FIG. 2.

chemical Society, it was pointed out that certain temperature determinations were made on amorphous and graphitic carbons which showed that the heat conductivity of the latter was, as might be expected, very much greater than that of the former. The measurement of heat conductivity is by no means easy, and what follows must be considered as merely a preliminary study of the subject, dealing, as it does, with the relative heat conductivities of the amorphous and graphitic forms of carbon.

In making the experiment, bars of carbon having cross-sections of 53 x 53 mm. and lengths of 750 mm. were heated at one end, by means of a lamp. Holes about 6 mm. in diameter

[1] Trans. Am. Electrochem. Soc., **11**, 317, *et seq.*

were drilled in the carbons at points distant 50 mm. from one another, and thermometers inserted in the holes. Preliminary experiments having shown that the emissivity of amorphous carbon was much greater than that of graphitic carbon, the emissivities were made approximately the same by polishing both carbons with graphite powder, so that they presented similar radiating surfaces. When the temperature conditions of the carbons had reached the steady state, readings of the thermometers in the holes and the temperature of the surroundings were taken. This is a very tedious determination and necessitates taking a very large number of readings, until it happens that the conditions are just right. Variations in the temperature of the surroundings are difficult to avoid, and variations in the lamp used for heating the end of the carbon cause waves of heat to travel along the bar, thus spoiling the determinations.

When a satisfactory set of readings is obtained, the excess of the observed temperatures over the surroundings is calculated and the curves plotted as shown in Fig. 2, where AB is the curve for a graphitic carbon bar and AC the curve for amorphous carbon.

According to the theory of this method, if a series of temperatures, t_1, t_2, t_3, etc., are observed, and the values, θ_1, θ_2, θ_3, etc., of the excess of each temperature over the surroundings is calculated, then these are connected by the following equations:

$$\frac{\theta_1 + \theta_3}{\theta_2} = \frac{\theta_2 + \theta_4}{\theta_3} = \frac{\theta_3 + \theta_5}{\theta_4} = \text{etc.}$$

In this particular experiment, the results shown in the following table were obtained:

	Amorphous Carbon.	Graphitic Carbon.
$\frac{\theta_1 + \theta_3}{\theta_2}$	2.310	2.008
$\frac{\theta_2 + \theta_4}{\theta_3}$	2.331	2.024
$\frac{\theta_3 + \theta_5}{\theta_4}$	2.327	2.021

	Amorphous Carbon.	Graphitic Carbon.
$\frac{\theta_4 + \theta_6}{\theta_5}$	2.234	2.031
$\frac{\theta_5 + \theta_7}{\theta_6}$	2.333	2.026

With the exception of one of the values for the amorphous carbon, these results are fairly good; but when the part of the bar is reached where the temperatures are nearly equal to the surroundings and the difference of temperature between consecutive holes is small, a slight error in the temperature readings makes a large difference in the value of the function.

If now the mean values of the functions obtained above are taken, and from these the relative conductivities of amorphous and graphitic carbon calculated, we find that

$$\frac{K_g}{K_a} = 18$$

where K_a is conductivity of amorphous and K_g the conductivity of graphitic carbon. If the temperatures in the first, third and fifth holes are taken, so as to eliminate the end holes where the determinations are not so accurate, we have

$$\frac{K_g}{K_a} = 18.5$$

It is not pretended that the results of these experiments are of any high order of accuracy, for it may readily be seen that important errors are possible. But, for the purpose in view, it did not seem necessary to spend the time and take the trouble necessary to obtain results of greater accuracy. The object of the investigation was to obtain data for estimating the heat losses in electric furnaces, and the determination of these must, at the best, be but approximate. As already observed, this experiment is only to be considered as a preliminary study of the heat conductivities of two important materials used in electric furnace construction. It is hoped, in the near future, to attempt making an approximate determination of the absolute

heat conductivities of carbon, and when this is done, it will probably be possible to make estimates of the heat losses through furnace terminals made of carbon.

FitzGerald and Bennie Laboratories,
Niagara Falls.

DISCUSSION.

Mr. Carl Hering: How does its heat conductivity compare with the heat conductivity of metals?

Mr. F. A. J. FitzGerald: I do not know. I have not been able to find any publications giving the heat conductivity of carbon. Undoubtedly such determinations have been published, but I do not know where to find them.

Prof. Jos. W. Richards: It might be interesting in this connection to know that I once asked Mr. Hall why he never tried to use graphitized carbons in his aluminium bath. He said they could not be used. I had not thought of the reason why: the graphitized carbons immersed in the bath conducted the heat away from the bath too rapidly.

Mr. Fred. Becket: The relative figures refer to room temperatures only. In electric furnace work you have to deal with relative conductivities at comparatively high temperatures.

Mr. FitzGerald: The figures given in the paper refer only to room temperatures and up to 100° C. In applying the exponential law on which the heat conductivity calculations are made it is assumed that there is no change in the heat conductivity of the material with change of temperature.

A paper read by Prof. S. A. Tucker at the Twelfth General Meeting of the American Electrochemical Society, in New York City, October 19, 1907; President C. F. Burgess in the chair.

GRANULAR CARBON RESISTORS.

By S. A. Tucker, A. Doty and R. W. Cauchois.

In the use of granular carbon for resistance material in the electric furnace, many varying conditions may exist, dependent upon the size of the carbon grain, the compression to which the grains are subjected, and the number of times the material has been employed for this purpose. It has always been noticed, in using the resistance type of electric furnace, that at the commencement of the run with new ground coke as the resistor, that although a very high e. m. f. is impressed across the terminals of the furnace, but little current flows, owing to the very high resistance of the "green" resistor material.

After a little while, the temperature of the furnace rises, and a larger quantity of gas and fumes is given off by the resistor. This condition prevails for some time, during which the resistance of the furnace and current flowing through varies very rapidly, and if a high enough e. m. f. is kept constantly impressed across the terminals, the temperature will steadily rise, until this gas period is passed and the rapid fluctuation of the resistance ceases. It will then be found that as the temperature increases, the resistance of the furnace slowly, but steadily, decreases, and if the impressed e. m. f. is not rapidly cut down, a large rush of current is liable to occur.

If, however, the resistor has been subjected to one thorough heating in which the carbon reaches a high degree of temperature, the conditions existing are far more uniform, which is due to the elimination of the volatile products from the coke by the preliminary heating.

Almost similar conditions prevail for direct or alternating currents, and it has been the purpose of this investigation to study these conditions, both with direct and alternating current, and also the influence of the size of the grains of which the resistor is composed.

The material used for the experiments was ordinary gas coke, which was roughly ground and then put through a series of sieves of 10, 20, 30, 40 and 50 meshes to the inch. The coke passing No. 50 sieve was labeled Grade 50; similarly, the coke retained between No. 40 and No. 50 sieves was labeled Grade 40.

The furnace for the experiment was constructed of "alberine" stone, with the exception of the end pieces, or electrodes (Fig. 1). On a base 9 x 13 x 1, 3/10 inches are placed two slabs to serve as side pieces and two electrodes of Acheson graphite, which occupy the ends. The dimensions of the sides were 13 x 2½ x

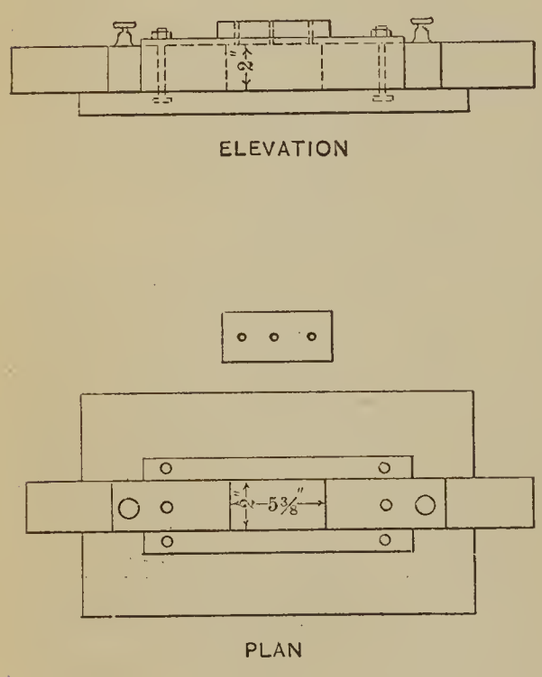

Fig. 1.

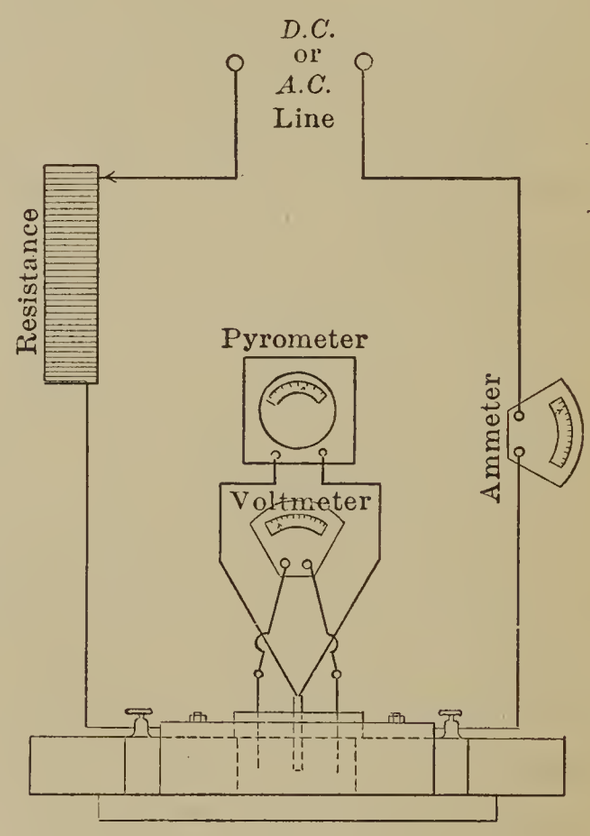

Fig. 2.

1, 3/10 inches. These were placed 2 inches apart and bolted to the base, the heads of the bolts being counter-sunk. At the ends are placed the two electrodes, with a face area of 2 x 2 inches. They occupy the entire space between the two side pieces, and thus a receptacle 5⅜ x 2 x 2 inches is formed, in which the resistor material is placed.

As a cover for this receptacle, a piece of "alberine" stone was used, which rested on the electrodes and exerted no pressure on the coke. Three holes were bored in the cover, one in the center, through which to place a thermometer or pyrometer tube, and two small ones 4 inches apart, to admit stout platinum wires,

in order to determine the voltage drop. The cover piece was 5¾ x 1 x 1 3/10 inches, thus just long enough to rest on the electrodes.

In the tests, in which the coke was subjected to pressure, a piece of stone, similar in every way except in length, was substituted. It was just long enough to extend between the electrodes, or 5⅜ inches, and on this was placed the desired weight, which was 10 pounds in these tests.

In every case the coke used was poured into the open space to the level of the top of the electrodes and carefully smoothed, so that the surface was uniform and no pressure existed on the carbon. In the experiments with pressure the smaller cover was used. The connections and auxiliary measuring instruments are shown in Fig. 2. For the lower temperatures a thermometer was substituted for the pyrometer shown. It was found necessary to use a voltage of 220 in order to get sufficient current through the circuit to show results.

EXPERIMENTAL.

Use of Green Coke.

In all experiments on green coke, direct current was used.

The first experiment was made with unused green coke, using grade No. 10. Starting with the current in the circuit one ampere, and keeping the voltage impressed on the circuit constant, the resistance of the coke, and therefore the current in the circuit, was allowed to vary. As the temperature rose, the resistance of the circuit commenced to vary rapidly, probably due to the gas period mentioned before. So rapidly did the needles of the voltmeter and ammeter fluctuate that no results of any value were obtainable.

As the temperature rose still further, fumes and some odor were given off, while the rapid fluctuations of the instruments continued. Readings were attempted every two minutes of the voltmeter, ammeter and pyrometer.

Although practically no results of much value were obtained, it was seen that the resistance of the coke increased with increasing temperatures, a fact exactly opposite of the results obtained in later tests with carbon from which the gases had been driven.

As the resistance went on increasing, the current, of course,

decreased, and after a time the temperature commenced to go down, when the run ceased. The resistance of grade No. 10, unpacked, and with no pressures upon it, at room temperature of 18° C., was found to be 75 ohms. The upper limit of the resistance was 220 ohms, at 87° C., when the temperature was decreasing.

Using grade No. 30, equally unsatisfactory results were obtained, the resistance at room temperature being 96 ohms, and the same phenomena of increasing resistance with increasing temperature occurred, except that for the first few readings the resistance decreased and then increased.

With grade No. 20, green coke, starting with 2 amperes, unsatisfactory results were again obtained, the resistance fluctuating rapidly, until apparently the temperature reached a point where the volatile matter had all been driven off, when the resistance commenced to decrease steadily, until at 1000° C. the resistance was 7.7 ohms, while at room temperature it was 59 ohms.

The following table gives the readings for this test:

TABLE I—GRADE NO. 20.

Variable Direct Current. Not Treated to Drive Off Volatile Matter.

	Current.	E. M. F.	Resistance.	Temperature.
	2	118	59	
(1)	3.80	76	20	205
(2)	2.70	105	39	438
(3)	3.15	85	28	715
	4.20	63	15	842
	4 70	55	11.10	890
	4.85	51.5	10.60	900
	5.00	57.5	10.30	913
(4)	5.15	50	9.70	927
	5.20	50	9.60	933
	5.30	50	9 45	937
(5)	5.45	50	9.20	949
	5.60	48	8 55	956
	5.75	46.5	8.10	970
	5.90	46	7.80	978
	6.05	47.5	7.85	994
	6.15	48.0	7.80	1,013
	6 20	48.5	7.84	1,020
	6.30	48	7.60	1,028
	6.35	49	7.70	1,034
	6.45	48	7.45	1,040

Time, one hour. Readings taken every three minutes.
At (1) smoke appeared at positive terminal.
At (2) this smoke became very marked.
At (3) smoke appeared at center.
At (4) smoke appeared at negative terminal.
At (5) all smoke stopped.

No tests were run on unused coke using alternating current, as the results attained with direct current were so uncertain that further tests were unwarranted.

Variable Current Tests, Volatile Matter Driven Off. Direct Current.

In starting an electric furnace of the resistance type, using granular carbon as the resistor, it is customary to impress quite a high voltage across the terminals and wait for the resistor to heat up and its resistance to fall, when a large current flows and the voltage may be cut down.

In the following tests the coke used was first subjected to a high temperature by making it the resistor in a separate electric furnace, until the volatile matter had been driven off, and after grading was placed in the apparatus before described, to be studied under varying conditions. Starting with Grade No. 50, and a current of 3 amperes, the resistance was found to be 6.3 ohms. Keeping the impressed voltage constant, the current in the circuit was allowed to vary. As the temperature rose the resistance fell steadily until the minimum point of 4.5 ohms was reached, when the temperature reached 376° C. Although the temperature increased steadily until 435° was reached, the resistance remained nearly constant, as shown in Table II.

The next test was run on Grade No. 40, under similar conditions to No. 50. The resistance decreased much more rapidly than in the case of the finer coke. In 28 minutes the resistance fell from 11 to 7.15 ohms, when the temperature was 405°. This test was carried on for 7½ hours (Table III). After about 30 minutes the resistance remained practically constant for approximately two hours, when, with the temperature still increasing, it started to increase. After some time of this increasing resistance, the temperature commenced to fall.

The next experiment was with Grade No. 30 (Table IV), similar conditions to the preceding, and was carried on for 3½

hours, when again the phenomenon of decreasing resistance with increasing temperature was noted up to a certain point, when, with the temperature still rising, the resistance also started to go up. This variation is clearly indicated in the table.

An experiment on Grade No. 20 (Table V), same conditions, further bore out the observations made for the other grades. Grade No. 10 (Table VI) also varied in the same manner.

A run was made on a mixture of all five grades (Table VII), equal parts, the conditions being the same as in the previous tests.

The phenomenon noticed in the separate grades was less marked, for both the first decrease of resistance under increasing tem-

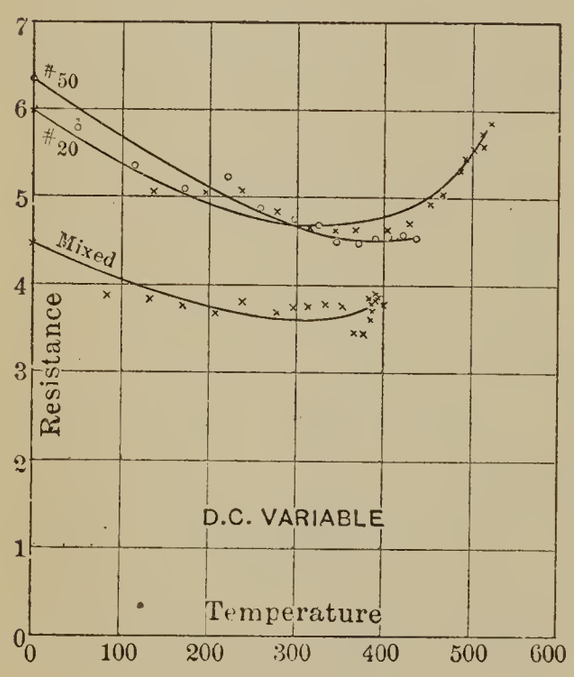

FIG. 3.

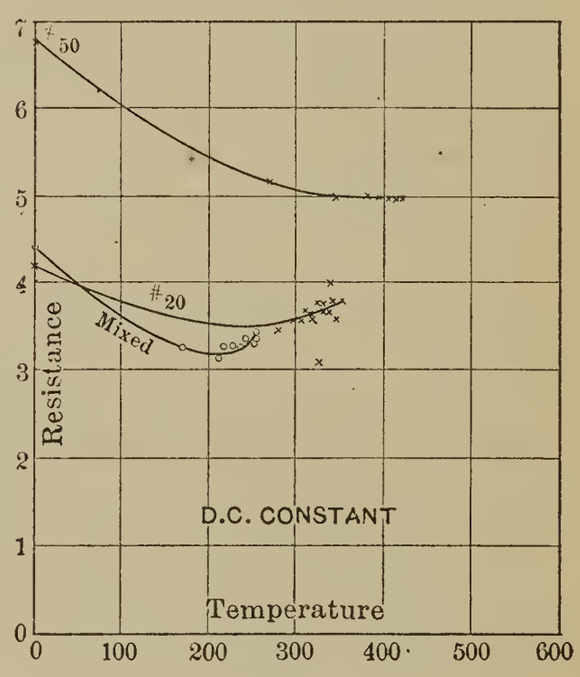

FIG. 4.

perature, and the point at which increased under increasing temperature.

Fig. 3 gives curves of resistance and temperature for grades Nos. 50 and 20, and a mixture of equal parts of all grades. In general it may be said that the resistance cold is greatest for the finer grades of coke, and for the same temperature a mixture of all grades was lowest in resistance. This is shown by the curves plotted for temperature and resistance (Figs. 3 and 4.)

The tables give some idea of the relative efficiency of the different grades for the energy necessary to reach a certain temperature.

At a temperature of approximately 370° it may be seen that the

mixture was taking 152 watts; Grade No. 20, 135 watts; Grade No. 50, 133 watts; but that it took the mixture 1 hour and 50 minutes to reach this temperature, it took Grade No. 20 1 hour and 10 minutes, Grade No. 50, 1 hour and 20 minutes.

Thus a tabulation of grades and watt-hours necessary to reach 370° would be:

Grade..	*Watt-Hours.*
Mixture	207
No. 50	131
No. 40	97
No. 30	76
No. 20	109
No. 10	103

indicating that Grade No. 30 is the most efficient from the results for this temperature. From Table V, we find that Grade No. 20, green coke, reached 370° using 24 watt-hours. It is unfortunate that so few accurate readings could be taken with green coke, as the results obtained pointed to the fact that this material is more efficient as a resistor material.

TABLE II—GRADE NO. 50.

Variable Direct Current. Volatile Matter Previously Driven Off.

Current.	E. M. F.	Resistance.	Temperature.
3	19	6.33	
3.55	19	5.35	115
3.95	20	5.10	172
4.30	22.5	5.23	224
4.65	23	4.89	260
4.95	23.5	4.75	300
5.10	24	4.70	325
5.28	24	4.55	350
5.43	24.5	4.51	373
5.55	25.2	4.54	395
5.64	25.8	4.58	407
5.68	26	4.58	422
5.74	26	4.54	435

Time, two hours. Readings taken every ten minutes.
Starting current, 3 amperes.

Table III—Grade No. 40.

Variable Direct Current. Volatile Matter Previously Driven Off.

Current.	E. M. F.	Resistance.	Temperature.
3	33	11	
3.75	31	8.40	255
4.18	31	7.40	360
4.55	32	7.00	416
4.78	33.5	7.00	469
4 92	3.49	7.05	508
5.15	3.65	7.08	540
5.40	3.80	7.04	600
5.47	3.86	7.05	622
5.46	3.90	7.14	645
5.38	3.99	7.42	655
5 32	4.00	7.51	660
5.29	4.05	7.65	665
5.23	4.08	7.80	678
5.17	4.10	7.93	681
5.09	4.12	8.10	687
5.10	4.15	8.14	693
5.00	4.15	4.3	690

Time, 3 hours. Readings taken every ten minutes.

Table IV—Grade No. 30.

Variable Direct Current. Volatile Matter Previously Driven Off.

Current.	E. M. F.	Resistance.	Temperature.
3	23	7.67	
3.65	20	5.48	116.7
4.15	20.80	5.01	240
4.65	21.5	4.63	292
4.95	23.5	4.75	345
5.38	24.1	4.48	290
5.75	25.2	4.39	438
5.90	26.2	4.44	480
6.10	28	4.59	501
6.23	29	4.65	530
6.35	30.2	4.76	560
6.35	31.8	5.0	575
6.45	32.9	5.1	590
6.50	33.5	5.15	603
6.50	35	5.39	620
6.51	36.10	5.54	635
6.44	37	5.75	642
6.42	38	5.92	650
6.29	39	6.21	663
6.31	40.3	6.40	704
6.25	40.1	6.42	705
6.15	41.1	6.69	700

Time, three and one-half hours. Readings taken every ten minutes.

TABLE V—GRADE NO. 20.

Variable Direct Current. Volatile Matter Previously Driven Off.

Current.	E. M. F.	Resistance.	Temperature.
3	20	6	
3.49	17.8	5.10	140
3.90	20	5.10	200
4.30	22	5.10	240
7.65	22.5	4.85	280
4.89	22.8	4.46	320
5.19	24	3.63	343
5.39	25	4.63	370
5.60	26	4.65	408
5.68	27	4.75	433
5.80	28.5	4.91	455
5.82	29.5	5.07	470
5.82	31	5.32	488
5.80	31.8	5.49	496
5.80	32.1	5.54	505
5.80	32.5	5.60	517
5.70	33	5.80	517
5.80	33.5	5.80	517
5.80	34	5.86	521

Time, three hours. Readings taken every ten minutes.
Starting current, 3 amperes.

TABLE VI—GRADE NO. 10.

Variable Direct Current. Volatile Matter Previously Driven Off.

Current.	E. M. F.	Resistance.	Temperature.
3	20.5	6.84	
3.85	19.0	5.35	125
4.50	20	4.44	205
5	21	4.20	240
5.50	22	4.00	290
6	23.5	3.92	335
6.50	25	3.85	370
6.40	26.5	4.14	408
6.30	28	4.45	430
6.25	28.5	4.57	440
6.35	30.7	4.84	452
5.80	30.5	5.26	473
6.05	30.5	5.04	477
6.25	31.5	5.04	485
6.25	32	5.13	500
5.90	32	5.43	508
6.10	33	5.41	510
5.80	34	5.86	514
5.85	34	5.82	510
5.80	34	5.87	514
5.80	36	6.20	522
6.00	34.5	5.75	532

Time, three and one-half hours. Readings taken every ten minutes.

TABLE VII—GRADE MIXED.

Equal Parts of All Grades. Variable Direct Current. Volatile Matter Previously Driven Off.

Current.	E. M. F.	Resistance.	Temperature.
3	13.5	4.50	
4.12	16	3.90	86
4 60	17.8	3.88	134
5.13	19.5	3.80	172
5.48	20.3	3.70	210
5.75	22	3.83	240
6.22	23	3.70	280
6.00	22.6	3.76	298
6.10	23	3.77	314
6.30	24	3.80	335
6.35	24	3.80	354
6.60	23	3.48	368
6 60	23	3.48	377
6.60	24	3.64	390
6.60	24.5	3.71	390
6.60	25.5	3.86	390
6.50	24.0	3.70	388
6.70	24.5	3.66	392
6.50	25	3.84	394
6.60	25	3.80	401
6.40	24.8	3.88	394
6.40	25	3.90	394

Time, three and one-half hours. Readings taken every ten minutes. Starting current, 3 amperes.

A comparison was next made with coke which had been twice heated to a high temperature with that which had been heated but once, to see if the further elimination of volatile matter had an influence on the results.

The coke which had been heated once was mixed, raised to a high temperature for the second time in a separate electric furnace, and after cooling was carefully graded. Grades Nos. 10 and 40 were selected and runs made on them as before, using direct current and allowing it to vary.

Tables VIII and IX give the results obtained. The conclusions to be drawn are that after a second heating the resistance of the material is lower than after one heating, the variation being about the same in both cases. The phenomena of at first having a negative temperature coefficient and then a positive coefficient

was again observed. Results indicate that the point of maximum efficiency is passed after the first heating of the coke. Thus it is shown that Grade No. 40 treated once to a high temperature to drive off volatile matter consumed 21.7 watt-hours in reaching a temperature of 280° C., while Grade No. 40, treated twice, consumed 83.5 watt-hours in reaching the same temperature.

Grade No. 10, once treated, consumed 25 watt-hours in reaching 205° C.; the same grade, twice treated, consumed 51.5 watt-hours in reaching this temperature.

These results indicate that twice-heated coke is less efficient than once-heated, for resistor purposes, and there is reason to suppose that green coke is still better.

TABLE VIII—GRADE NO. 40.

Variable Direct Current. Twice Treated to Drive Off Volatile Matter.

Current.	E. M. F.	Resistance.	Temperature.
3	14.5	4 80	
3.51	15	4.28	85
4	16.4	4.10	138
4.40	17 5	3.98	177
4.78	18.7	3 91	210
5.02	19 5	3.88	240
5.18	20	3.86	270
5 50	21	3.86	298
5.70	22	3.76	330
5.80	22	3.79	348
5.95	22.5	3.78	365
6.10	23.5	3.85	390
5.85	23.5	40.2	405
5.80	24.2	4.11	403
5.82	24.6	4.23	405
5.68	24	4.23	405
5.90	24.7	4.18	413
5.85	25	4.28	415
5.90	25.2	4.27	420
5.85	25	4.27	422
5.88	25.2	4.26	430
5.85	25.2	4.28	437

Time, three and one-half hours. Readings taken every ten minutes.

TABLE IX—GRADE NO 10.

Variable Direct Current. Twice Treated to Drive Off Volatile Matter.

Current.	E. M. F.	Resistance.	Temperature.
3	11	3.66	
4.15	12	2.79	70
4.85	13	2.68	112
5.50	14.3	2.60	145
5.75	15	2.61	172
6.40	16	2.50	205
6.80	17	2.50	270
7.15	17.7	2.48	296
7.30	18	2.46	314
7.32	18.5	2.53	321
7.38	18	2.44	340
7.30	19.5	2.77	344
7.28	19.7	2.71	344
7.28	19.8	2.72	348
7.00	19	2.72	355
6.90	20	2.90	355
6.60	19	2.88	355
6.55	18.5	2.82	348
6.55	19	2.90	353

Time, three hours. Readings taken every ten minutes.

Variable Alternating Current. Volatile Matter Driven Off.

The same procedure as before was next gone through with, using alternating current instead of direct. It was found, however, that starting with 3 amperes did not give enough temperature range to show results, so a starting point of 5 amperes was used. All the tests with alternating current were made upon coke which had been twice previously heated to drive off volatile matter, and at a different starting point than the variable current tests with direct current, so that no comparison is possible between the direct and alternating current tests using variable current.

Comparisons, however, may be made between different grades, using alternating current. Tables X, XI and XII show the results for Grades No. 50, No. 20 and a mixture of equal parts of all grades. In each case it may be seen that the resistance decreased to some extent at first as the temperature increased, and then commenced to increase with further rise in temperature.

This variation is not exactly like that of some of the same grades

using direct current shown by comparison of tables and curves. The peculiar results in this particular series of tests is partly accounted for by the fact that there was overheating in the balancing rheostat which caused a fall in voltage. For this reason the results are of small value.

It was thought possible that the frequency of the current might have an effect, and in order to determine this point a series of tests

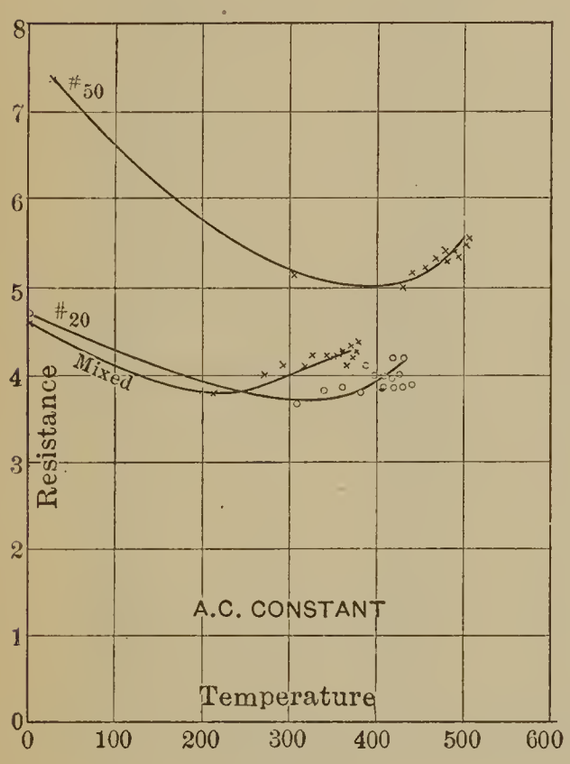

FIG. 5.

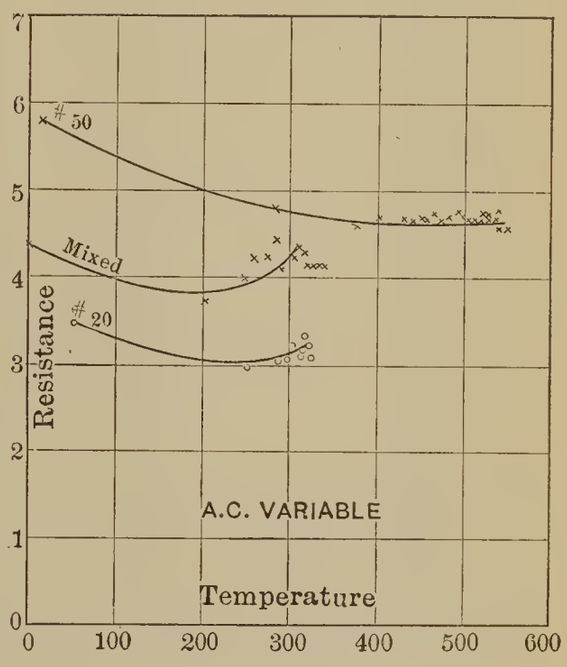

FIG. 6.

were run using a frequency of 57 instead of 128, as employed at first.

The results obtained in each case were practically the same as for the higher frequency, except in the case of Grade No. 20, where a lower resistance was shown all through the test, probably due to some slight difference in pressure, naturally a cause which would tend to give this result. In general, the tests showed that the frequency had no effect on the variation.

TABLE X—GRADE NO. 50.

Variable Alternating Current. Volatile Matter Previously Driven Off.

Current.	E. M. F.	Resistance.	Temperature.
5	29	5.80	200
5.21	24	4.60	372
5.20	25	4.80	288
5.15	24.25	4.70	401
5.20	23.80	4.57	422
5.20	24.40	4.70	431
5.25	24.50	4.65	441
5.20	24.50	4.70	452
5.20	24.50	4.70	460
5.25	25	4.75	465
5.50	25.50	4.64	478
5.40	25.30	4.70	485
5.40	25.75	4.76	495
5.50	26	4.70	500
5.60	26.25	4.68	507
5.55	25.90	4.67	512
5.60	26.20	4.68	517
5.60	26.50	4.73	522
5.65	26.80	4.75	523
5.67	26.50	4.68	530
5.75	27	4.70	538
5.75	27.10	4.70	538
5.80	27.50	4.75	540
5.95	27.30	4.60	545
6.00	27.50	4.58	551

Time, four hours. Readings taken every ten minutes.

TABLE XI—GRADE NO. 20.

Variable Alternating Current. Volatile Matter Previously Driven Off.

Current.	E. M. F.	Resistance.	Temperature.
5	17.50	3.50	50
5	15	3	251
5	15.50	3.10	286
5	15.50	3.10	297
4.88	15.60	3.19	301
4.80	15.50	3.24	305
4.85	15.50	3.20	305
5.00	15.70	3.14	314
5.00	16.00	3.20	314
4.75	15.90	3.35	319
4.80	15.50	3.24	319
4.88	15.75	3.25	319
4.90	15.80	3.23	319

Time, two hours. Readings taken every ten minutes.

Table XII—Grade Mixed.

Equal Parts of All Grades. Variable Alternating Current. Volatile Matter Previously Driven Off.

Current.	E. M. F.	Resistance.	Temperature.
5	22	4.40	
5	18.8	3.76	205
4.75	19	4.00	250
4.48	19	4.24	260
4.50	19.1	4.29	275
4.43	19.9	4.49	287
4.60	19	4.13	294
4.50	19.6	4.35	310
4.65	20	4.30	317
4.75	19.7	4.16	322
4.80	20	4.17	330
4.70	19.5	4.15	335

Time, two hours. Readings taken every ten minutes.

Constant Current Tests.

(a) Direct Current.

In order to compare definitely alternating and direct current results, a series of runs was made, starting with 5 amperes and keeping this current absolutely constant and maintaining the run until an approximately constant temperature was reached.

The following tables show the results obtained. Using direct current first, it is evident, in the case of Grade No. 50, that the resistance first decreased and then increased to a certain point and from then remained constant, though the temperature rose further for some little time.

A mixture of all the grades showed about the same variations. Grade No. 20, however, was somewhat irregular, but in the main showed the same tendency as the other grades.

As to energy conditions. It took the mixture 108 watt-hours to reach a temperature of 250° C., while Grade No. 20 reached this temperature in less than 30 watt-hours, and Grade No. 50 reached it in less than 25 watt-hours. Grade No. 50 took 46 watt-hours to reach 343° C., and Grade No. 20, 230 watt-hours to reach this temperature, results which conflict with those obtained with variable current.

Table XIII—Grade No. 50.

Constant Direct Current. Volatile Matter Previously Driven Off.

Current.	E. M. F.	Resistance.	Temperature.
5	34	6.80	
5	26	5.20	200
5	25	5.00	343
5	24.9	4.98	370
5	25	5.00	380
5	25	5.00	394
5	25	5.00	405
5	25	5.00	405
5	25	5.00	410
5	25	5.00	412
5	25	5.00	412
5	25	5.00	418
5	25	5.00	418

Time, two hours. Readings taken every ten minutes.

Table XIV—Grade No. 20.

Constant Direct Current. Volatile Matter Previously Driven Off.

Current.	E. M. F.	Resistance.	Temperature.
5	21	4.20	
5	17.5	3.50	232
5	17.5	3.50	280
5	18	3.60	297
5	18	3.60	305
5	18.5	3.70	310
5	18	3.60	318
5	18.2	3.64	316
5	19	3.80	325
5	18.5	3.70	331
5	18.5	3.70	332
5	20	4.00	339
5	18.5	3.70	340
5	18.3	3.60	342
5	19	3.80	352
5	19	3.80	361
5	19	3.80	361

Time three hours. Readings taken every ten minutes.

TABLE XV—GRADE MIXED.

Equal Parts of All Grades. Constant Direct Current. Volatile Matter Previously Driven Off.

Current.	E. M. F.	Resistance.	Temperature.
5	22	4.40	
5	16.8	3.30	170
5	16.1	3.20	207
5	16.5	3.30	220
5	16.5	3.30	226
5	16.8	3.30	233
5	17	3.40	240
5	17	3.40	241
5	17	3.40	251
5	17	3.40	252
5	17	3.40	252
5	17.5	3.50	252
5	17.4	3.48	252
5	17.1	3.42	252

Time, two hours. Readings taken every ten minutes.

(b) Alternating Current.

A similar set of tests was next made, using alternating current at a frequency of 128. The current in the circuit was maintained constant at 5 amperes, and the test continued until a constant temperature was reached. Tables XVI, XVII and XVIII and the curves show the results obtained, which are approximately the same as those for direct current, Tables XIII, XIV and XV. A comparison of watt-hours required to reach a temperature of about 340°, between alternating and direct current, would be as follows:

A. C.		*D. C.*	
Watt-hours.	Grade.	Watt-hours.	Grade.
38	No. 50.	46	No. 50.
35	No. 20.	230	No. 20.

Table XVI—Grade No. 50.

Constant Alternating Current. Volatile Matter Previously Driven Off.

Current.	E. M. F.	Resistance.	Temperature.
5	36.50	7.30	30
5	26.00	5.20	305
5	25.30	5.06	401
5	25.00	5.00	430
5	25.80	5.16	440
5	26.10	5.22	454
5	26.60	5.32	466
5	27.65	5.41	478
5	26.80	5.36	485
5	27.20	5.44	491
5	27.00	5.40	496
5	27.50	5.50	500
5	27.80	5.56	501

Time, two hours. Readings taken every ten minutes.

Table XVII—Grade No. 20.

Constant Alternating Current. Volatile Matter Previously Driven Off.

Current.	E. M. F.	Resistance.	Temperature.
5	23.5	4.70	
5	18.5	3.70	305
5	19.1	3.82	340
5	19.4	3.88	358
5	19.3	3.86	380
5	20.5	4.10	387
5	20	4.00	397
5	20	4.00	405
5	19.6	3.92	406
5	20	4.00	412
5	19.6	3.92	412
5	20.1	4.02	418
5	19.9	3.98	422
5	19.5	3.90	425
5	21	4.20	420
5	21	4.20	420

Time, two and one-half hours. Readings taken every ten minutes.

TABLE XVIII—GRADE MIXED.

Equal Parts of All Grades. Constant Alternating Current. Volatile Matter Previously Driven Off.

Current.	E. M. F.	Resistance.	Temperature.
5	23	4.60	
5	19	3.80	211
5	20	4.00	270
5	20.5	4.10	290
5	20.5	4.10	314
5	21	4.20	322
5	21	4.20	340
5	20.9	4.18	340
5	21	4.20	346
5	21.1	4.22	352
5	21.4	4.28	356
5	21.5	4.30	356
5	20.8	4.16	367
5	21.2	4.24	371
5	21.4	4.28	372
5	21.9	4.38	373

Time, two and one-half hours. Readings taken every ten minutes.

A set of tests was made, using various grades of coke under a pressure of 10 pounds. The results seemed to indicate that the only change caused by pressure was a considerable decrease in the resistance of the resistor.

Because of the low resistance not much temperature variation was obtainable with the current possible to work with in the small experimental furnace used for this work, the results are, consequently, of little importance.

Interpretation of Results.

The results obtained seem still to leave it an open question whether a resistor material of high or low resistance would give most efficient results. In fact, the design of the furnace might decide this question, or whether the machine furnishing the power was designed for low voltage and heavy current, or *vice versa.*

From the tests, using variable direct current, the conclusion might be drawn that a certain grade of coke was more efficient than another, and then in a further test using constant current this result is contradicted. Also, the tests using alternating cur-

rent would seem to indicate that a greater efficiency is obtainable with this than with direct current.

It would appear as a result of this investigation as if the more frequently the coke is used the less degree of temperature is obtainable for the same expenditure of energy.

A result shown throughout the experiments proves that the coarser the grade of coke the greater its conductivity.

Another result indicated is that any single grade of coke is more efficient than a mixture of all grades.

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DISCUSSION.

PROF. JOS. W. RICHARDS: I should like to ask what quantity of material was treated in these tests, and is the amount of heat energy required to obtain a certain temperature roughly proportional to the quantity of materials?

PROF. S. A. TUCKER: Approximately the same volume of material was treated each time, the dimension of the opening being constant, but I do not remember exactly what the quantities were. It was a rather small space.

PROF. RICHARDS: It seems to me as if an explanation is needed as to why a mixture of various sizes should require so much more watt-energy to reach a certain temperature, and my impression is that it is because the mixture packs closely, and so there is more weight of material in a given space. The void spaces in a space occupied by material whose particles are of uniform size is some 35 per cent. of the whole space, the variation not being large for different sizes of material, but when graded materials of different sizes are mixed together, the smaller pieces fit in between the larger ones, so that the percentage of void space may be reduced to 10 per cent., or even less, and, therefore, you have considerably greater weight of material when it is of mixed sizes in a given space, than when it is of one size. If we had the data we might calculate whether the heat energy required to bring the contents up to a certain temperature was proportionate to the different weight of material packed in, in the different cases.

A paper read at the Twelfth General Meeting of the American Electrochemical Society, in New York City, October 18, 1907; President C. F. Burgess in the chair.

SILICON MONOXIDE.

By Henry Noel Potter.

Theoretically, silicon, like carbon, should have a monoxide, as well as a dioxide, but in the case of silicon only the dioxide has been recognized.

Clemens Winkler attempted to form silicon monoxide,[1] and reports: "It is supposed that SiO does not exist, for even in heating a mixture of SiO_2 and Si, the reaction

$$SiO_2 + Si = 2SiO$$

does not result."

As this experiment was performed in a combustion furnace, under conditions where the maximum temperature probably did not exceed 1000° C., the conclusions based thereon can only be accepted within the temperature range involved.

If the Winkler experiment be extended to temperatures attainable with ease in the electric furnace, a brisk reaction takes place, with liberation of a brown smoke which burns to silicon dioxide. If the reaction is effected in an inert atmosphere, in a furnace of the resistance type the smoke can be collected as a soft, brown, very fine and voluminous deposit upon all exposed surfaces within the furnace.

In the following table, the analyses of samples of this brown deposit are given, together with data regarding the ratios of silicon and silicon dioxide in the charge.

[1] Ber. Chem. Ges., 23, 2657.

Table I.

Resistance Furnace Runs.

36 kw. Three min., after gradually heating up during two min. thirty sec. Resister 10 inches long, 5/8 inch square section of Acheson graphite.

No.	Silicon.		SiO_2		Si % in Charge.	% Si Analysis.	Calculated SiO in Product.
	Weight.	Mesh.	Weight.	Mesh.			
1	28	$\frac{60}{100}$	60	$\frac{60}{100}$	63.7	62.04 61.26	89.7 85.0
2	28	$\frac{60}{100}$	30	$\frac{60}{100}$	72.4	63.37 62.24	97.6 91.0
3	28	$\frac{60}{100}$	15	$\frac{60}{100}$	81.5	68.19 69.50	87.5 83.7
4	28	$\frac{60}{100}$	120	$\frac{60}{100}$	56.8	67.75 65.84	88.7 94.0
5	28	$\frac{60}{100}$	240	$\frac{60}{100}$	52.3	60 42 63.00	80.0 95.5
6	28	100	60	$\frac{40}{60}$	63.7	62.22 64.62	91.0 97.5
7	28	$\frac{60}{100}$	60	100	63.7	67.17 65.33	90.5 95.5
8	28	Ball Mill	60	$\frac{40}{60}$	63.7	61.58 63.40	87.0 98.0
9	28	$\frac{40}{60}$	60	Ball Mill	63.7	65.56 66.66	95.0 91.8

In the weight columns are given the relative weights of silicon and silica. In the columns headed "mesh" are given two numbers, the smaller indicating the number of mesh per linear inch through which the material was screened, and the larger numbers indicating the number of mesh per linear inch on which it was collected.

TABLE II.

Analysis of Materials Referred to in Table I.

	A	B	C	D	E	F	G	H	J
No. in Table I.	Sample.	Insoluble in 1NaOH + 10H_2O in 1 Minute.	Dissolved.	Impurities in Final SiO_2.	Impurities Al_2O_3 & Fe_2O_3 Recovered.	Total Dissolved Material Containing Si.	Corrected Weight SiO_2 from (F).	Si in (G).	(H) ÷ (F).
	Grams.	Grams.	Grams.	Grams.	Grams.	Grams.	Grams.	Grams.	% Si.
1	1.0049	0.0247	0.9802	0.0058	0.0035	0.9709	1.2813	0.6023	62.04
	1.0002	0.0202	0.9800	0.0078	0.0045	0.9677	1.2611	0.5928	61.26
2	0.5727	0.0160	0.5567	0.0048	0.0046	0.5474	0.7379	0.3469	63 37
	0.5602	0.0184	0.5418	0.0043	0.0055	0.5321	0.7045	0.3312	62.24
3	1.0226	0.0970	0.9256	0.0151	0.0067	0.9038	1.3110	0.6163	68.19
	1.0012	0.1180	0.8832	0.0085	0.0018	0.8729	1.2883	0.6056	69.50
4	0.9555	0.0415	0.9140	0.0035	0.0061	0.9045	1.3036	0.6128	67.75
	1.1006	0.0389	1.0617	0.0053	0.0056	1.0508	1.4718	0.6919	65.84
5	0.9246	0.0445	0.8801	0.0073	0.0043	0.8685	1.1163	0.5248	60.42
	1.1037	0.0466	1.0571	0.0095	0.0028	1.0448	1.4002	0.6582	63.00
6	1.1348	0.0638	1.0710	0.0176	0.0072	1.0462	1.3848	0.6510	62.22
	0.9366	0.0404	0.8962	0.0070	0.0018	0.8874	1.2198	0.5734	64.62
7	1.0307	0.0661	0.9647	0.0066	0.0042	0.9539	1.3625	0.6405	67.17
	0.9175	0.0462	0.8713	0.0108	0.0079	0.8526	1.1842	0.5567	65.33
8	0.9704	0.0282	0.9422	0.0132	0.0013	0.9277	1.2152	0.5712	61.58
	0.9418	0.0271	0.9147	0.0042	0.0050	0.9055	1.2212	0.5741	63.40
9	1.0094	0.0456	0.9638	0.0114	0.0032	0.9492	1.3237	0.6223	65 56
	0.9797	0.0405	0.9392	0.0297	0.0045	0.9050	1.2833	0.6033	66.66

As shown in Table II, impurities have been deducted, and the total silicon calculated in per cent. of the total silicon-oxygen content. The method of analysis has been elaborated by Mr. A. B. Albro, who will himself describe it.

It will be observed that the silicon ratio is close to 64 per cent., the theoretical silicon content of silicon monoxide, and is but slightly influenced by large changes in the ratio of silicon to silica in the reacting charge.

Before declaring that the reaction

$$Si + SiO_2 = 2SiO$$

has here been realized, two objections must be met.

First, it might be thought that the reaction was wholly between the carbon and the resistor of the furnace and the silica of the charge, and that the free silicon itself took no part in it.

There is ample evidence against this. First, the amount of powder produced exceeded in weight the amount which could be accounted for by the loss in weight of the resistor. Second, there was but little carbon monoxide gas given off, whereas a large volume would have been produced had the total weight of powder been due to the reduction of silica by carbon. The measurement of the amount of gas given off was not made quantitatively, but it was estimated from the increase in pressure within the furnace indicated by the vacuum gauge. A small vacuum pump was kept operating during the run, and in the case of runs where the reaction was really between carbon and silica, the pump was not sufficiently large to maintain a high degree of vacuum, owing to the rapid liberation of gas. The vaccum remained high when running with silicon and silica as a charge.

A second objection might be urged, that perhaps no inter-reaction at all took place, and that both silicon and silica were distilled, side by side, without reacting upon each other.

The evidence against this may be gathered from comparing run No. 2, Table I, where but half the theoretical amount of silica is present, with run No. 5, where four times the normal amount of silica is present, the average of the two analyses of No. 2 being 62.80 Si, and the average of No. 5 being 61.71 Si, thus showing little or no influence due to any change of mixture proportions, which would almost certainly manifest itself in the case of parallel distillations from granular mixtures.

Further evidence against mere distillation was gathered by trying a run with the resistor surrounded by silicon only, no silica being present. The result was negative, silicon not being sensibly volatile at the temperatures involved.

Runs were also made with a shield of granular silicon next to the resistor, and a mixture of silicon and silica around this. These runs gave practically undiminished yields of material of the same composition, although in this case the silica could not come in contact with the carbon, and the reaction must have been between silicon—which could not volatilize—and silica.

No temperature measurements were made in the case of the

resistance furnace operating under reduced pressure in an inert atmosphere, but from experiments subsequently made, in a tube furnace, it is thought that at temperatures between 1700° and 1800° C. the reaction between silicon and silica is quite brisk. As silica is somewhat volatile within this range and at higher temperatures, the product should contain an excess of oxygen, because some unchanged silica will accompany the products of reaction.

The proof, therefore, seems conclusive that silicon can and does reduce its own dioxide, with the production of a lower oxide, which analysis indicates to be the monoxide. As high temperature products are usually characterized by simplicity of composition, as pointed out by Moissan, the formula may be assumed to be SiO.

If carbon or silicon carbide be used as a reducing agent in place of silicon, the brown powder is produced in voluminous quantities. An arc furnace can be substituted for the resistance furnace, and the yield per unit of electrical power employed considerably increased. With increased heat concentration, however, the amount of silica distilled appears to be increased as the percentage of total silicon in the brown powder decreases.

An illustration of this, Table III, shows analyses of material made in an arc furnace, the charge material being leached, Corning sand and leached, purified graphite. The leaching was done with concentrated reagents calculated to leave as nearly pure SiO_2 and pure carbon as is possible with the commercial materials used.

TABLE III.

Run No.	Charge.	Percentage of Si in Product After Deducting Impurities.
1	$2SiO_2 + C$	56.95
2	$3SiO_2 + 2C$	57.83
3	$3SiO_2 + 4C$	56.98
4	$SiO_2 + 2C$	56.13

The percentage of silicon is seen to be practically independent of the proportion of carbon to silica in the charge, and this is thought to be evidence that the composition of the product depends on the temperature at which the furnace is run, which determines the ratio of silica distilled to silica reduced.

While the proportion of silica to reducing agent has practically no effect upon the proportion of silicon in the product, it nevertheless has a considerable influence upon the yield. This is shown in the following table of furnace runs.

TABLE IV.

Runs were made by pumping out to 29¼ inches, then washing twice with hydrogen to 24 inches, pumping out to 29¼ inches, cutting off vacuum, and beginning run, letting vacuum fall to 0, then opening cock, allowing run to continue at atmospheric pressure, pumping out when run was over. Barometer 30 inches.

No. of Run.	K. W.	K. W. H.	Total Yield Grams.	Grams per K. W. H.	Charge Mixture.
1	20	.2	37 5	18+	$4SiO_2 + SiC$
2	20	2	26.0	13	$3SiO_2 + SiC$
3	20	2	42 0	21	$2SiO_2 + SiC$
4	20	2	27.5	13+	$SiO_2 + SiC$
5	20	2	12.5	6+	$SiO_2 + 2SiC$

It will be observed that the highest yield is with run No. 3, the mixture proportions of the charge corresponding to the formula

$$2SiO_2 + SiC = 3SiO + CO.$$

In Nos. 1 and 2 the silica is in excess. In Nos. 4 and 5 the silicon carbide is in excess. In each case the yield is reduced.

Table V shows some observations made in runs where the reducing agent was purified carbon.

TABLE V.

Runs were made by pumping out to 29¼ inches, then washing twice with hydrogen to 24 inches, pumping out to 29¼ inches, cutting off vacuum, and beginning run, letting vacuum fall to 0, then opening cock, allowing run to continue at atmospheric pressure, pumping out when run was over. Barometer about 30 inches.

No. of Run.	K. W.	K. W. H.	Total Yield Grams.	Grams per K. W. H.	Charge Mixture.
1	20	2	50.0	25	$2SiO_2 + C$
2	20	2	64.0	32	Intermediate
3	20	2	88.5	44	$SiO_2 + C$
4	20	2	49.5	24+	Intermediate
5	20	2	43.0	21+	$SiO_2 + 2C$

It will be observed that the highest yield here also corresponds to the theoretically-correct mixture for the production of SiO, namely

$$SiO_2 + C = SiO + CO.$$

In view of the chemical analogy between carbon monoxide and silicon monoxide, it would seem theoretically possible that, even though silicon monoxide does exist as such at electric furnace temperatures, nevertheless, on cooling it would dissociate in accordance with the formula

$$2SiO = SiO_2 + Si.$$

An investigation of the brown powder shows that it is attacked by hydrofluoric acid with a liberation of a material which is much richer in silicon than the original brown material, though we have never been able to produce pure amorphous silicon in this way. However, the fact that part of it is dissolved and part not might seem to indicate the separation of chemically different substances, but this is not certain, because the action of the hydrofluoric acid might be to effect dissociation of a true silicon monoxide molecule, with the liberation of silicon.

An analogy to such an action may be found in the case of siloxicon, which is reputed to be a true chemical compound,

but which nevertheless is attacked by hydrofluoric acid with liberation of amorphous silicon carbide.

A great deal of chemical investigation was gone through with, to find, if possible, some property of the brown powder which should be different from any possible property of a mixture of silicon and silica.

It was thought for a time that such a property had been discovered when it was found that the brown powder, when freshly prepared, dissociates water with the liberation of hydrogen. This reaction takes place slowly with ice water, and is brisk with boiling water. The evolution of gas, however, soon ceases, due, doubtless, to the coating of silica produced upon the particles by the reaction.

It was subsequently found, however, that both crystalline and amorphous silicon have this property of dissociating water, provided the surfaces of the particles have not had opportunity of becoming covered with a protecting film which they soon acquire on exposure to the atmosphere.

This property of silicon can be quite readily shown by dissolving off the film with hydrofluoric acid and after washing off the acid in cold water, throwing the now active silicon particles into boiling water. In the case of finely granular silicon, the hydrogen liberated will adhere to the particles and float them up to the surface.

The matter of the thickness of the film, in the case of silicon, was investigated, and the result may be of interest here. Silicon of great purity was ground in a pebble mill for about six weeks, then floated in water, and such portion as remained suspended for twenty-four hours was separated out and used for the test.

This very fine silicon was leached successively in hydrochloric acid, aqua regia, hydrofluoric acid. It was then washed in water, alcohol and ether, and dried, and a weighed sample repeatedly subjected to the action of anhydrous hydrofluoric acid at a temperature slightly above 100° C. The reaction may be expressed as follows:

$$SiO_2 + 4HFl = SiFl_4 + 2H_2O \text{ (gas)}.$$

The water liberated is in the gaseous state, and is so rapidly removed by the gas current as not to be able to react with the

exposed silicon surfaces. It was found that during the cooling, which occurred in an air-filled desiccator, the particles of the sample coat themselves with the film, which is removed on the next application of the acid.

Successive weights, therefore, give the loss of weight due to the removal of the film, and this was found to be approximately 0.1 per cent. of the weight of the sample. Assuming the particles to be cubes 0.001 millimeter on a side, the minimum thickness of the film may be calculated equal to about

$$1.6 \times 10^{-7} \text{ of a millimeter.}$$

This is a thickness which is small, even in comparison with a length of a single wave of violet light. The presence of this film doubtless underlies the successful application of silicon crystals as receivers for wireless telegraphy.

We have never succeeded in finding any chemical test to distinguish silicon monoxide from a mixture of silicon and silica, such as would be produced from the dissociation of silicon monoxide.

While it is of no practical industrial importance as yet determined, whether the brown powder is or contains true silicon monoxide or whether it is entirely dissociated into a mere mixture, it was thought of sufficient theoretical importance to justify a further investigation. It would appear that chemistry may not be able to distinguish between a compound and a mixture under such conditions as we have here presented, and therefore the distinctions should be sought by methods which reveal the energy relations of the component atoms.

The first investigation along this line was to measure the heat of combustion of the brown powder in a special bomb calorimeter, which has been described by the writer before a former meeting of this society.[2] (See cut, page 200.)

The heat of combustion observed must be due either to the combustion of

$$2Si + 2O_2 = 2SiO_2,$$

or

$$2SiO + O_2 = 2SiO_2.$$

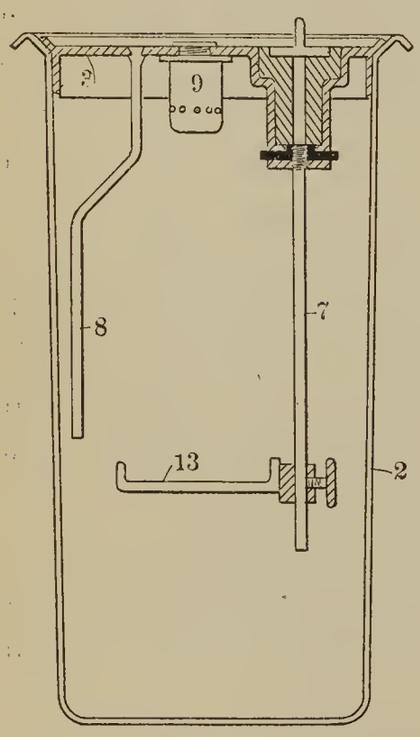
In the former case, the heat of combustion should be that of

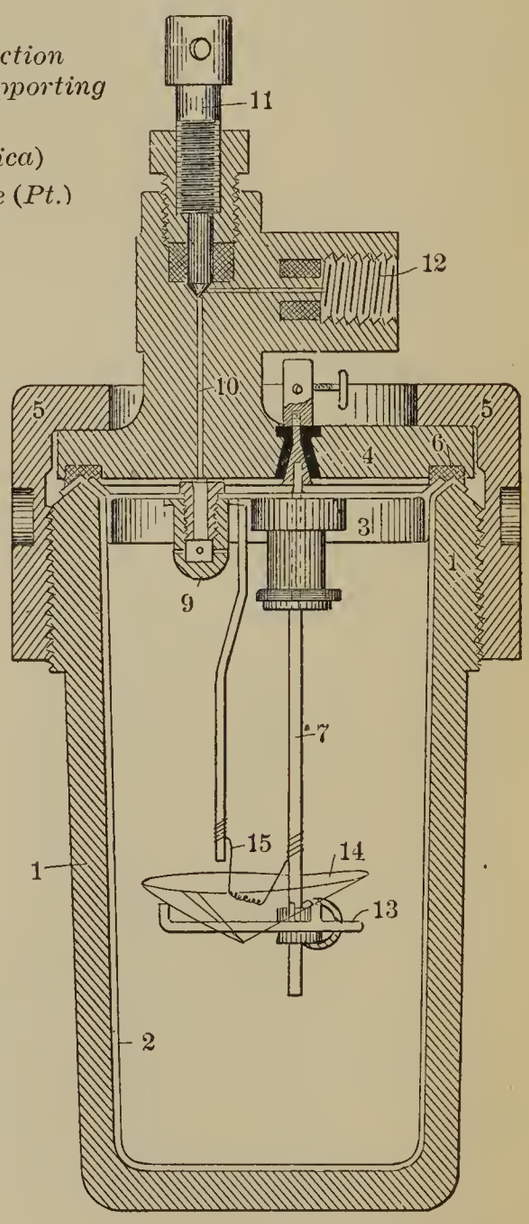
[2] A Bomb Calorimeter for Use With Substances Whose Oxides are Solids, Henry Noel Potter. Trans. A. E. S., Vol. XI, 1907.

amorphous silicon; in the latter, it may be different just as the combustion of two molecules of carbon monoxide yields more heat than the combustion of one atom of carbon.

The method of procedure was to calculate the observed heat as though it were due to the burning of silicon. If the resulting

1. *Outer Shell*
2. *Inner Shell* } *Lining*
3. " *Top* }
4. *Cover*
5. *Clamping Ring*
6. *Lead Gasket*
7. *Crucible Support (insulated)*
8. *Grounded Connection*
9. *Gas Inlet Baffle*
10. *Inlet Hole*
11. *Inlet Valve*
12. *Tank Connection*
13. *Crucible Supporting Ring*
14. *Crucible (Mica)*
15. *Igniter Wire (Pt.)*





heat of combustion is too high or too low by an amount impossible to explain by errors of observation, the inference is that the combustion was not of silicon, and must therefore have been of silicon monoxide.

Incidentally, it was necessary to redetermine the heat of combustion of amorphous silicon, to have the comparison based

on results determined in the same apparatus and under the same conditions.

In addition to this, an artificial mixture of amorphous silicon and silica was made up in such a proportion as to imitate the composition of silicon monoxide, and the heat of combustion of this mixture observed. Such a mixture may be termed a pseudo-monoxide.

Finally, a brown, vitreous material, similar to that exhibited to this society by Mr. F. J. Tone at the Boston meeting, in 1905, was very finely pulverized and its heat of combustion determined. It will be remembered that the analysis of this material corresponded in silicon-oxygen ratio to the theoretical monoxide, but that Mr. Tone stated that after adequate examination it appeared to be only a mixture.

In the following table will be found the results of the calorimeter determinations:

Table VI.

Bomb Calorimeter Determinations.

No.	Material.	Gram Calories per Gram Silicon—Burned.		Remarks.
1	Si Amorph.	7593	Avg. 7532	This was material made by Vigoroux process. Vid. Dammer, Handb. d. anorg. Chem. (1903), p. 371.
2	"	7647		
3	"	7540		
4	"	7398		
5	"	7483		
6	Si Amorph.	7882	7841	This was material made by Woehler process.
7	"	7848		
8	"	7792		
9	Si Crystal.	7595		Average of 5 determinations, Trans. A. E. S., Vol. XI, p. 263.
10	Si Amorph.	7719		Troost & Hautefeuille, Watt; Vol. IV, p. 445.
11	Si Crystal.	7432		
12	Pseudomonoxide	7800		Woehler: Si Amorph + Fine Purified SiO_2 (28:60)
13	Brown Vitreous Material	7439		
14		7663		
15		7226		
16		7206		
17	Brown Powder	8038	8079	Si + SiO_2 reaction, see Tables I and II
18	"	8155		
19	"	8072		
20	"	8050		
21	"	8054	8158	Small Arc Furnace Material (New York)
22	"	8357		
23	"	7957		
24	"	8265		
25	"	8659	8527	Large Arc Furnace, Regular yield (Pittsburgh)
26	"	8412		
27	"	8511		
28	Si Amorph.	7444	7438	Si made from treating Brown Powder with HFl.
29	"	7432		

The corrections due to impurities have not been attempted, as the values of the heat of combustion of SiC and of $FeSi_2$ are not accurately known. They are both stable compounds, and must have a considerable positive heat of formation. In the case of $FeSi_2$, the heat of combustion of the iron and silicon as such can only reach about 4,700 calories per gram, and after deducting the heat of formation of $FeSi_2$ must be still lower.

In the case of SiC, the sum of the heats of the silicon and carbon, as such calculates 7,745 calories per gram. The heat of formation must be high, as in three attempts to burn it in the bomb only one succeeded partially, about half the charge only being burned. The heat rise was too small to base any reliable determination upon.

An attempt was therefore made to form SiC from Si + C in the bomb, and determine directly the heat of formation. This was successful in getting SiC and a reliable rise in temperature. The determination of the residues was so difficult and contained so many chances of error that no great confidence is felt in the result. The result calculated was

Heat of combustion of elements Si + C	7,745	calories per gram
Heat of formation of SiC	5,972	calories per gram
Difference, or heat of combustion of SiC	1,773	calories per gram

It thus appears that the heats of combustion of the samples of brown powder are lower than if they were corrected for impurities. It may be interesting to follow this through a single case, to determine roughly the probable extreme of error possible.

ANALYSES OF MATERIAL USED IN TABLE VI. No. 17-No. 20.

		Analysis No. 1.	*Analysis No. 2.*
1.	Original sample	0.99985 grams.	1.00115 grams.
2.	SiC contained	0.0211 "	0.0249 "
3.		2.11% (average 2.30%)	2.49%
4.	Fe_2O_3 found	0.0061 grams	0.0076 "
5.	$FeSi_2$ calculated	0.0086 "	0.0108 "
		$(FeSi_2 = \frac{255.6}{160} \times Fe_2O_3)$	
6.	Al_2O_3 found	0.0031 grams.	0.0038 grams.
	$Al_2O_3 + FeSi_2 + SiC$	0.0328 "	0.0395 "
		0.0099 "	0.0132 "
7.	Undissolved SiO_2	(See method of analysis.)	
8.	Total foreign matter	0.0427 grams.	0.0527 grams.
9.		=4.27%	=5.27%
10.	Corrected dissolved matter	0.95715 grams.	0.94845 grams.
11.	Weight SiO_2 recovered	1.31010 "	1.28605 "
12.	Si — equivalent	0.61600 "	0.60470 "
13.	Si in $FeSi_2$	0.0043 "	0.00540 "
14.	Difference	0.61170 "	0.59930 "
15.	No. 14 ÷ No. 10 —	63.9%	63.2%
	Average		63.55%
	Theoretical Si in SiO		63.94%

The sample contained an average of 0.97 per cent. of $FeSi_2$.

Determination No. 19, Table VI, was made with 0.6725 grams of brown powder, containing .97 per cent. $FeSi_2$ equals 0.00652 grams capable of a maximum heat liberation of 30.6 calories, and containing 2.3 per cent. SiC equals 0.0155 grams capable of an estimated heat liberation of 27 calories. The heat due to impurities equals 27 + 31 = 58 calories.

The total heat observed was.....	1,924	calories
Deduction of heat impurities.....	58	"
Due to combustion of Si or SiO.....	1,866	"

The increase of weight due to burning 0.0065 grams $FeSi_2$ equals 0.0052 grams.
The increase of weight due to burning 0.0155 grams SiC equals 0.0077 grams.
The increase of weight due to impurities equals 0.0129 grams.

Total observed increase of weight....	0.2686	grams oxygen
Deduction caused by impurities.....	0.0129	" "
Increase due to Si or SiO.....	0.2557	" "

Silicon equivalent $\frac{28.4}{32} \times 0.2557 = 0.2270$ grams Si burned.

Heat of combustion calculated as due to

Si $\frac{1866}{0.2270}$ equals	8,220 calories per gram
Tabular value..	8,072
Difference due to impurities....	148 cal., or 1.8 per cent.

A total impurity of the character shown by analysis of 2.3 + 0.97 = 3.27 per cent., produces a decrease in the heat of combustion calculated as due to burning of Si of 1.8 per cent. It is thought, therefore, that the influence of impurities may be neglected, as the object is merely to show that the heats observed are too high to be reasonably ascribed to the combustion of silicon.

It will be observed in the foregoing table (VI) that amorphous silicon produced by the Vigoroux process has a heat of combustion which is very close to that of crystalline silicon as determined by the writer, also very close to the amorphous

silicon which results from treating the brown powder with hydrofluoric acid.

It may be noticed that the heat of combustion of Woehler amorphous silicon and of crystalline silicon, as determined by the writer, both lie roughly 100 calories per gram higher than the corresponding values determined by Troost and Hautefeuille.

It will be seen that practically no difference is produced in the observed heat of combustion of the Woehler amorphous silicon when the latter is mixed with fine purified silica in such proportion as to imitate the composition of silicon monoxide. As might be expected, therefore, the presence of the silica is without effect on the heat of combustion.

The heat of combustion of the brown powder when calculated as though due to the combustion of silica is higher by 200-800 calories per gram than can be accounted for by the combustion of any known form of silicon. The silicon resulting from treating brown powder with hydrofluoric acid shows a lower heat of combustion even than the ordinary amorphous silicon. This would indicate that the latter silicon was not present in elemental form in the brown powder.

On the whole, it appears that the heat of combustion of the brown powder varies from sample to sample, but that it is consistently higher than can be explained on the basis of the combustion of silicon in any known form.

It would not appear that we have a hitherto unknown form of amorphous silicon present, as this would be separated by the hydrofluoric acid treatment, and should then show the same heat of combustion as the brown powder from which it was made. There may be said, therefore, to be presumptive evidence of the existence of silicon monoxide in the brown powder.

In the brown, vitreous material, however, there is no such evidence, and it appears, therefore, that Mr. Tone was correct in assuming this to be a mixture, and not a compound.

For the sake of completeness, I may add that the brown, vitreous material, if used by itself as a charge, in a furnace, gives the brown, powdered material, as might be expected.

Before leaving the vitreous material, however, I wish to call attention to one of its peculiarities, namely, that it has a well-defined color which is perfectly uniform throughout the mass.

There is, however, another vitreous material, which is found in the furnace near the brown, vitreous material. This second material is of a variable purple color, but when examined under the microscope, it is found to contain minute globules of crystalline silicon imbedded in the normal brown vitreous material.

This is considered to be evidence that the brown vitreous material has a very good chemical reason for containing the same amount of silicon as the theoretical monoxide. This reason is that it was monoxide at a high temperature, and in cooling off slowly has completely dissociated.

Wherever there is any free silicon present, this collects by itself, separating from the monoxide and forming the globules referred to. This would indicate that the dissociation temperature of silicon monoxide lies below the melting point of silicon, which is near 1400° C. for chemically-pure silicon, and somewhat lower for commercial silicon containing several per cent. of dissolved metallic impurities, usually iron and aluminum.

The difference which has been shown to exist between the brown vitreous material and the brown powder can be plausibly explained as due to the difference in the conditions surrounding their formation.

The furnace in which the brown powder is now made is the latest of a number of experimental devices, all having the same characteristics, namely, an arc between two opposed horizontal carbon electrodes in a closed chamber, consisting of a body containing the charge and a cover of considerable volume. There are a great many refinements which have suggested themselves during the course of experiments, but a complete description must be reserved for another occasion. The theoretically important conditions are that the charge should surround the arc, that the arc should not be buried too deeply beneath the upper surface of the charge, that the hollow space or crater which forms about the arc when it operates shall soon work to the surface of the charge and break through into the empty space above, forming a discharge throat, and finally, that this empty space shall be large enough and so shaped that the bounding walls nowhere approach the throat near enough for the highly-heated blast of gas therefrom to strike them.

When the furnace has been in operation sufficiently long for

the crater to have formed a throat, and the normal process to be in operation, the reaction occurs on the inner walls of the crater. The silicon monoxide is apparently released in the gaseous state, enabling it to rush out of the crater almost instantly, along with the liberated carbon monoxide. Once out of the throat, the gases expand very rapidly and are instantly chilled, so that the silicon monoxide does not have time to completely dissociate before it is brought down to a temperature at which its speed of dissociation is practically zero, all of which is in strict analogy with the known dissociation phenomenon of carbon monoxide, the only difference being that silicon monoxide happens to be a solid, and not a gas, at ordinary temperatures.

It would appear that silicon monoxide is a sublimate, as the author has not been able to liquefy it in a tubular resistance furnace at a temperature of 1,700° C.

The brown vitreous material is apparently produced by the cooling of gaseous silicon monoxide upon the walls of small passages through the charge material in the furnace, and owing to its slow cooling, dissociation has ample time to become complete.

The deductions outlined above have received a curious confirmation in a study of the specific heats of the various substances herein considered.

In the case of an ordinary substance obeying the law of Dulong and Petit, it would be impossible, by a comparison of specific heats, to determine whether the substance examined were a mixture or a compound, but silicon does not follow this law, but has a specific heat which within ordinary temperature ranges is too low, but which grows higher and higher with increased temperature.

Silicon dioxide follows the abnormal character of silicon in its specific heat, indicating that whatever the cause of the change of the specific heat of a silicon molecule on cooling, it applies also to the silicon within the silica molecule.

It has been supposed that compounds consisting of relatively few atoms have a specific heat which is an additive function of the heats of their component atoms, but that where abnormal heat capacity is shown, that this is due to some change in the molecular structure. This is almost the only clue we have to

structural changes occurring within the molecule of solid substances.

It seemed possible that in the case of silicon monoxide, which is normally a high-temperature compound and exists at ordinary temperatures only by virtue of an accident of cooling, that the molecular structure must preserve the peculiarities of the normal high temperature condition, and that the specific heat of such a compound should be higher than that of the mixture resulting from dissociation.

To investigate this, a very accurate calorimeter was designed, with a view of eliminating sources of heat loss when operating with finely-powdered substances. This apparatus was checked by determining the specific heat of several well-known substances, and also by having the heat of amorphous silica in granular form determined by the United States Bureau of Standards, for comparison with the determinations made by us.

A good many refinements were introduced as a result of work with the apparatus, and a very high degree of dexterity was acquired by those operating the calorimeter, so that results could be confirmed with an adequate degree of accuracy. The results are collected in Table VII.

Table VII.

Specific Heat Determinations.

No.	Substance.	Specific Heat.	Remarks.
1	Pure Silver	0.0559	Bunsen (Smith'n Phy. Tab.)
2	"	0.0553 (30°–98.4° C.)	
3	"	0.0559 (32°–98.85° C.)	
4	Aluminum	0.2135 (20° C.)	Naccari (Smith'n Phy. Tab.)
5	"	0.2211 (100° C.)	
6	"	0.2136 (31°–98.5° C.)	
7	"	0.2155 (32°–98 55° C.)	
8	SiO_2 Amorph.	0.1892	U. S. Bureau of Standards.
9	"	0.1860	
10	"	0.1854	
11	"	0.1915 } Avg.	
12	"	0.1905 } 0.1886	
13	"	0.1897	
14	Si Amorph.	0.1892	Woehler process material
15	"	0.1859 } 0.1880	
16	"	0.1889	
17	Pseudomonoxide	0.1800	Woehler Si(amorph.), 28 p'ts
18	"	0.1823 } 0.1828	Fine purified SiO_2, 60 parts
19	"	0.1862	Theoretical by Kopp's Law, 0.1888
20	Brown Vitreous	0.1850 } 0.1833	
21	Material	0.1815	
22	SiO_2 Crystal	0.1900 (30°–100° C.)	Average of 3 determ. on Corning sand, 99+% SiO_2
23	Quartz	0.1735 (0° C.)	Pionchon (Smith'n Phy. Tab.)
24	"	0.2786 (300° C.)	
25	"	0.305 (400°–1200° C.)	
26	Si Crys. Fused	0.1798	Purified, fine powdered, free from SiC
27	Si Crystal	0.1360 (–40° C.)	H. Weber, Chem. Kal. 1906
28	"	0.1833 (57° C.)	
29	"	0.2029 (232° C.)	
30	SiC Amorph.	0.1894	Average of 4 determ. made from Siloxicon
31	SiC Crys.	0.1857	Average of 3 determ.
32	Siloxicon	0.1911	

No.	Substance.	Specific Heat.	Remarks.
33	Brown Powder.	0.2014	Sealed in *glass* container
34	"	0.2028	
35	"	0.2063	No. 34 to No. 37 are repetitions of No. 33
36	"	0.2066	
37	"	0.2091	
38	"	0.1929	After heating No. 37 1 hr. at 400° C. redetermination of No. 38
39	"	0.1969	
40	"	0.1897	After heating again 1 hr. at 400° C. redetermination of No. 40
41	"	0.1900	
42	"	0.1885	After heating again 2 hrs. more at 400° C. Total heating 4 hrs. at 400° C. Weight of sample + container constant throughout
43	"	0.1880	
44	"	0.1893	
45	"	0.2147	Another sample in a *silver* container. No. 46 to No. 48 are redeterminations of No. 45
46	"	0.2062	
47	"	0.2110	
48	"	0.2193	
49	"	0.2024	A third sample (in glass). After heating No. 49 2½ hrs. at 400° C. Weight constant throughout
50	"	0.1862	

NOTE.—All measurements on Brown Powder are between 30° and 99° C. approximately.

In this table, the specific heats determined for silver, aluminum and amorphous silica are in such close agreement with the accepted values that there is no reason to question the substantial accuracy of the apparatus.

The surprisingly high values determined in the case of the brown powder, coupled with the lower values obtained for the same powder after it has been heated, would seem to point to a molecular change, which can be readily explained as a dissociation, in accordance with the theory already outlined.

The determinations were made in glass and confirmed in silver, thereby eliminating any possible influence of the container.

After the brown powder has been heated, the specific heat agrees closely with that of the brown vitreous material and with the pseudo-monoxide. This furnishes another ground for agreeing with Mr. Tone that the brown vitreous material is a mixture, and not a compound.

All measurements were made between room temperature of about 31° C. and about 98.5° C., as obtained in a steam bath. The thermometers used were of the Beckmann type, corrected

by comparison with a standard checked by the United States Bureau of Standards, and also corrected for errors of bore.

The constants of the apparatus were determined with great care, and the usual barometric and radiation corrections applied with care commensurate with the great accuracy of the instruments used.

It seems, in view of the foregoing, that adequate evidence has been collected, proving the existence of silicon monoxide at high temperatures, and indicating beyond a reasonable doubt that this compound may also exist at ordinary temperatures, if cooled with sufficient rapidity to escape dissociation.

It is thought that some dissociation is bound to occur, so that the brown powder, made as described, presumably consists of silicon monoxide and an indefinite amount of amorphous silicon and silicon dioxide, resulting from the dissociation of some monoxide. Also, in the product as commercially produced by reduction of silica with carbon and silicon carbide in an arc furnace, there is present a certain amount of silica resulting from the direct distillation of this compound. Finally, there is usually some amorphous silicon carbide present, and traces of metallic impurities from the materials used in the furnace charge.

To the brown powder the name "monox" has been given, this name covering the material in the dissociated, as well as in the undissociated, condition, inasmuch as there is no industrial distinction between the two, as yet determined.

The chemical properties have already been touched on. In general, they are conditioned by the presence of a film of silica over the particles, so that until this film is removed the properties are those of silica.

The specific gravity determinations are grouped in the following table:

TABLE VIII.

Specific Gravities.

No.	Material.	Specific Gravity.	Remarks.
1	Si Amorph.	2.194	Clemens Winkler (Watt's Dict. Chem.)
2	"	2.197	
3	"	2.214	Corrected results on material made by treating Monox with HFl
4	"	2.204	
5	"	2.35	Vigoroux (Watt's Dict. Chem.)
6	SiO_2 Amorph.	2.2	Watt's Dict. Chem.
7	Brown Powder	2.24	As produced impure 23° C.
8	"	2.191	As SiO after correcting for impurities
9	Brown Vitreous	2.266	F. A. J. FitzGerald
10	"	2.215	As Si + SiO_2 after correcting for impurities

The color when dry is a light yellowish brown, when wet with water or oil, a darker shade of light brown. The higher the refractive index of the wetting liquid, the darker the brown. Probably the darkest brown and true color would be seen when the powder is wet with a liquid having the same index as the silica film.

The size of the ultimate particles is very small, it being of the same order as those of soot or carbon blacks.

The heat insulating and electrical insulating properties are high. It is remarkably negative when electrostatically charged by friction. This property, however, seems to depend on fineness of particle, or extent of surface, polished glass being positive toward rough glass or powdered glass, as noted by early natural philosophers.[3] This has not been adequately studied in the present case.

The brown powder is extremely opaque, both dry and wet, a property that harmonizes with the idea of perhaps a partial dissociation, and therefore the presence of an electric conductor, namely, silicon. It is not thought that any weight can be laid on opacity as an evidence of complete dissociation, as partial dissociation would give the observed effect, to say nothing of the large number of opaque insulating substances.

[3] Deschanel's Nat. Phil. (1884), p. 550.

Monox has a number of interesting and important industrial applications, which will be made the subject of a separate communication.

I wish here to express my great indebtedness to Mr. George Westinghouse, for whom the foregoing research has been carried on, for his patience and continued interest during the long period over which it has extended.

Among my assistants, particular mention is due Mr. A. Bliss Albro, for many careful analytical determinations, as well as effective executive work in directing the efforts of others; Mr. Ernest M. Swett, for the bomb calorimeter work and calibration of thermometers, and for his work with Messrs. Ames S. Albro and J. M. Finch on the specific heat calorimeter.

DISCUSSION.

PROF. JOS. W. RICHARDS: I did not understand what the heat of combustion of silicon monoxide was determined to be.

DR. H. N. POTTER: We cannot say what the true heat of combustion of silicon monoxide is, because we have never had it absolutely and certainly separate from every other combustible substance. We can only say that the combustion of SiO to SiO_2 liberates more than half as much heat as the combustion of Si to SiO_2. This would indicate that the combustion of Si to SiO liberates less heat than that of SiO to SiO_2, which can be explained by assuming that energy is absorbed in disrupting the silicon molecule. However, we know very little about the structure of the solid molecule. It is only occasionally we get a suggestion of its possible nature.

DR. W. R. WHITNEY: One point occurs to me. While I see no reason for doubting the existence of the monoxide, it might be worth while to call attention to the fact that a mixture of silicon and silica, no matter what proportions of the two ingredients are used, might distil to what is practically a homogeneous product.

DR. POTTER: I appreciate the point of distilling in proportion to the relative vapor tensions, but I think Dr. Whitney has overlooked the fact that we also tried to distil silica by itself, but without appreciable yield.

DR. WHITNEY: I was under the impression that silicon was distilled. I withdraw my objection.

Prof. S. A. Tucker: What is the lowest temperature of dissociation? Four hundred degrees is mentioned; is that the lowest temperature of dissociation?

Dr. Potter: We have not made any attempt to discover at what temperature dissociation begins. I think that that would be a very difficult matter to determine in a case where the only clue to dissociation is a change in the specific heat. Heating rapidly to 100° C. appears to affect complete dissociation in about four hours. It would seem, therefore, that the speed of dissociation is quite slow at 400°, and may be assumed to begin a little below 400.

Dr. Chamblis: Does Dr. Potter doubt the existence of purely amorphous silicon?

Dr. Potter: No, nor of the existence of several kinds of amorphous silicon. There may be a whole series of amorphous forms of silicon, just as there is of amorphous carbon and of graphite and perhaps of diamond. In fact, there appears to be several varieties of crystalline silicon. Two forms of amorphous silicon would probably differ in their heats of combustion by as large an amount as the difference between amorphous and crystalline silicon. The point is that if we assume that a new form of amorphous silicon is present, this new form must be left after removing the silica with hydrofluoric acid. The heat of combustion of the residue after treating brown powder with HFl is not as high as known forms of amorphous silicon, whereas it should be higher to explain the observed heat of combustion of the brown powder.

Dr. Chamblis: Would it not be possible for us to have a mixture of some form of silicon and silica?

Dr. Potter: No. In order to settle that question, we treated the brown powder with hydrofluoric acid and determined the heat of combustion of the residue, and found it different from and lower than the heat of combustion of the brown powder calculated as silicon. The observed heat is always calculated as though it were due to the combustion of silicon, and this gives results which are persistently too high to be accounted for by the combustion of the residual silicon made from the brown powder itself (which must be the particular form of silicon present, if silicon be present at all). The inference is that the abnormal heat is due to the combustion of something not silicon. The only other substance that can burn to SiO_2 is SiO.

A paper read at the Twelfth General Meeting of the American Electrochemical Society, in New York City, October 18, 1907; President C. F. Burgess in the chair.

MONOX.

By Henry Noel Potter.

The new product, "monox," to which your attention is here directed, is an extremely fine, silky-feeling, light-brown, opaque powder.

In composition, there are reasons for believing it a mixture of silicon monoxide, silicon and silica, usually with a small content of silicon carbide and some metallic impurity.

The individual particles are of about the same size as those of lamp black, and are thus far smaller than the average particles produced by any process of grinding.

The true density of monox is about 2.24, but it is so voluminous as to weigh, when simply shoveled into a box, only about 2½ pounds per cubic foot.

It may thus seem to fill over 50 times the space it really occupies.

When fresh, it may easily be set on fire, and then burns with a twinkling, creeping combustion, without flame, slowly through the mass, giving much heat but little light. After standing, it becomes difficult to ignite in air, but may always be burned in oxygen.

On exposure to the atmosphere, an extremely thin film of silicon dioxide forms over the particles, giving them complete inertness to further atmospheric attack.

When fresh, it dissociates water with liberation of hydrogen, but this is soon at an end, due to the formation of the silica film.

It is completely soluble, save for certain impurities in hot dilute caustic solutions of NaOH or KOH, with liberation of much hydrogen and production of alkaline silicates.

It is attacked by both aqueous and anhydrous hydrofluoric acid, leaving a residue containing much amorphous silicon and some silicon oxide, perhaps so surrounded by silicon as to be protected

from the acid. It is difficult, in this way, to get a product analyzing over 90 per cent. silicon.

Hydrofluoric acid to which an oxidizing agent, such as nitric acid, has been added dissolves monox completely, except for any SiC contained. Hydrofluoric acid containing the fluoride of certain metals, such as mercury, silver and copper, which are reduced by nascent hydrogen will have these metals liberated in an extremely fine state of subdivision, and almost instantly, when monox is added to the solution.

Mixtures of monox and chemically weak oxides, like red lead and litharge, and particularly peroxides, react when ignited with the liberation of considerable heat.

This is about the limit of reactions with usual substances.

In general, toward all acid and neutral solutions and toward gases, particularly sulphur gases, it is inert, as might be assumed from its protecting film of silica.

Monox is perfectly non-poisonous and safe to handle. It is, however, not pleasant to breathe when suspended as dust in the air of a room, as it dries the throat and nasal passages.

It is readily wet with water and most other liquids, and adheres to them so tenaciously that they are not completely driven out at temperatures much above the boiling point. For example, monox wet with water can only be dried to constant weight at a temperature but little short of red heat.

Gases are occluded powerfully, especially at low temperatures. The Dewar experiment of producing a high vacuum by cooling charcoal in a closed vessel by liquid air can be repeated with monox in place of charcoal, the absorption being, however, somewhat slower with monox.

Dry monox is powerfully, negatively, electrostatically charged on the slightest provocation, such, for example, as drawing it suspended in dry air through a short rubber pipe. When so charged, it flies and adheres to all non-conducting surfaces, such as a cotton or other fabric, and in this way it can be filtered out of air or other gas in which it is suspended, and accumulates as a layer over the fabric, without caking together and without materially hindering the passage of gas.

Such a screen, coated with adhering monox, is impervious to fine solid particles of any sort, such as those constituting cigar

smoke or the fine particles formed when gaseous ammonia reacts with gaseous hydrochloric acid. Germs and all such organisms are stopped, so that air drawn through such a screen is sterile. This is a broad field of application and has not been thoroughly investigated as yet.

Monox has in a remarkable degree the power of thickening fluids with which it is mixed, and this, together with its chemical inertness, its opacity, and its pleasant light color, render it a very valuable pigment in certain oil paints, in particular paints for brick work and paints for protecting structural iron from rusting.

In the following table are given the relations by weight and by volume of various pigments and raw linseed oil, when mixed into paints of good thickness, to spread properly.

PIGMENT RATIOS.

No.	Pigment.	Sp. Gr.	Approx. % in Paint by Wt.	Approx. % in Paint by Vol.	Weight in lbs. Per Gallon.
1	White Lead	6.43	80	36.6	21–24
2	Red Lead	8.53	88+	45.4	30–35
3	Zinc Oxide	5.60	57+	18.1	14.8
4	Iron Oxide / Indian Red	4.32	64+	27.5	15.6
5	Ochre	2.97	50	25.7	11.8
6	Monox	2.2	20	10.2	8.6

Monox paint, owing to its extremely high oil ratio, can be used with advantage thicker than the painter is accustomed to handle. The drag of the brush, even with the thicker paint, is far less than with heavier pigments. The opacity is so high that the paint can be "stretched" over a large area and will still "cover," though it is self-evident that what is gained in area covered is sacrificed in thickness of the paint film, so that too great stretching is not consistent with the greatest durability.

There is a recognized, but not sharply defined, relation between the ratio of oil in a paint and the durability in average service. The optimum seems to lie in pigment enough to cover and viscosity enough to permit of a coat as thick as will dry smooth and properly. As between two inert pigments, the one requiring the more oil will be the softer, more elastic, more glossy, and probably more durable, if exposed only to usual atmospheric influences.

The lead pigments and zinc oxide are, however, not inert, and their durability is affected by other conditions beside those applying to inert pigments.

In paints designed to protect iron from rusting, the optimum is probably a paint of high volumetric oil ratio, great opacity, with a chemically inert and electrically non-conducting and very finely subdivided pigment.

The coating of a conducting particle of pigment with a film of oil should render it not-conducting, but it would seem safer to use a non-conducting, rather than merely a not-conducting pigment.

In view of the slight, but positive, permeability of paint films for moisture, the presence of a conducting particle is almost certain somewhere to establish contact electrically with the iron, with the formation of an electrochemical couple.

In the case of coarse pigments, a single pigment particle may extend nearly through the paint film, and in the case of certain earthy pigments, at least, establish a local porosity through the pigment particle.

In the case of chemically active pigments there are two classes, those which react with the atmospheric reagents, and those which react with the oil. Zinc oxide is an example of the former, and lead pigments of the latter.

These reactions, particularly the former, are accompanied by volumetric changes in the film, which increase its permeability sooner or later.

Neither zinc or lead paints are as bad as they might be expected to be, because the bad qualities of each are in a measure offset by other positively good qualities. Nevertheless, it is thought, and this is borne out in tests of more than average service severity, that the inert pigment paints are the best rust retarders.

Paints of considerable translucence are not serviceable, as sunlight in the presence of moisture is very active in promoting rusting. This can be shown in the case of transparent paint films made of the purest and best ingredients thickened with transparent filler, such as silica.

Such films will protect iron for months in an atmosphere saturated with moisture and artificially loaded with carbon

dioxide, in the dark. They will even grow mould on their surfaces and the iron beneath will remain bright. Such plates can be alternately subjected to the moisture-saturated atmosphere nights and to dry air daytime; as long as the light is subdued, they may not rust, but put them out in the sun and let them take the ordinary variations of moist and dry, hot and cold, dark and light, and they usually rust with great rapidity very uniformly on the upper surfaces, and very little on the under surfaces, which are in the shadow.

A test was made in which plates were coated one-half with transparent paint in which there was 30 per cent., by weight, of fine silica and 70 per cent., by weight, of linseed oil, the other half with an opaque paint, in which 6 per cent. of monox was present in place of some of the silica. The plates were exposed in the testing racks on the roof, and the transparent side rusted and pitted over its entire surface, while the other side showed no signs of rusting. For such reasons, it appears that opacity in a rust-retarding paint is essential.

Finally, the high oil ratio paint has more material to wear out before its cohesive strength is exhausted. The pigment in any paint only remains on the job as long as the oil is there to hold it, and oil gradually oxidizes to a crumbly mass which weathers away.

Therefore, with certain reservations necessary in any general statement concerning such a complicated subject as the weathering of paint, the paint having the highest volumetric ratio of oil should be the most durable, whether on iron or wood or stone.

In all these respects, monox is excellent, and in direct competition with other pigments has shown most gratifying durability.

The tests are made on sheet-iron plates bent into a half-cylinder, hollow side up, and fastened in a frame a few inches above the roof of a building, where they are subjected to rain, the full glare of the sun, the heat from the tin roof, steam, smoke and fine cinders. The trough-like shape favors the guttering action so fatal to paint films, while every angle, from almost vertical to horizontal, occurs somewhere on the plate.

This was designed to be the most severe test, representing only service conditions, that is possible, and from the rapidity with

which paints of accepted reputation break down, it would appear that the method is a great success.

Under such conditions, certain well and favorably-known rust-resisting paints were tested. They all show rust through two coats in a few months, while a paint of 20 weights of monox in 80 weights of raw linseed oil, with manganese drier, is much more durable; even a single coat has a record of eight months, although single coats are in general worthless, as they are a test of painting, rather than of paint, and usually fail, because of brush lines or other accidents.

In fact, the test of a really good paint is a matter of such duration that accident is very likely to play a large, if not deciding, rôle in the results. However, most paints are not good paints, so the field can be rapidly narrowed to a few really excellent mixtures, among which those containing monox will certainly be prominent.

A limited similarity exists between paint and printing ink, but this is more apparent than real. In a general way, the similarities lie in the chemical, the differences in the physical properties.

Paints are most largely used in light colors, whereas black inks outweigh all others put together. White lead is the pigment most used in paints, where carbon blacks are relatively little used. The reverse is true in inks.

Were monox not only opaque, but white in color, its effect would be revolutionary in paints. In inks, its color is of no importance, being completely masked. It depends for its value on other properties entirely.

As a matter of fact, the problem of making a good ink is simpler than the making of a good paint, at least when the cost is not the chief consideration.

However, there are very real problems in making ink, as a good ink must do a variety of seemingly contradictory things.

There are, aside from the color of an ink, certain properties of internal friction, cohesiveness, adhesiveness, and surface tension, which, taken together, make the "working qualities" of an ink. When the working qualities are in proper balance, the ink acts well on the press and it "prints"—that is, it goes on to the paper in a way to meet the printer's idea of technical excellence.

It is often impossible to define in scientific terms just what

excellence in an art may involve. The printing art is one of great refinement of detail, and a technical phraseology has grown up to express the various peculiarities and requirements.

The contribution of monox to a black printing ink containing it is to make the ink "lay" perfectly and dry with a dead, lustreless black which will not easily "offset,"[1] and thus does not require "slip sheeting."[2] It will not separate out of the varnish and lodge in the services between adjacent printing surfaces, and will, to a large extent, hinder other substances from so doing. In other words, it will not "fill up."

An explanation of the idea involved in an ink "laying" properly goes to the foundation of the art of half-tone engraving, and involves differences in papers which cannot be fully considered here. In brief, it is required that fine dots separated by wide spaces, coarse dots separated by narrow spaces, and large surfaces with no spaces, shall all receive ink in proper amount and shall transfer this to the paper with such evenness that a magnifying glass will discover neither "mottling" or "flooding" in the "solids," nor too great or too little intensity in the "mediums."

This may, perhaps, be expressed by saying that an ink "lays," which gives the same smooth impression from any sized surface, no matter how large or how small, from one a foot square to the smallest half-tone dot, and will do this time after time.

It appears that while there are a great variety of carbon blacks, which differ in color, fineness, and several other properties, no single black and no combination of blacks will give an ink which lays quite ideally or which is quite black.

The color is always improved in higher grade inks by adding a blue or purple "toning" color, and these "toners" help to make the ink lay in some cases; but, as their function is to color the ink, the amount introduced must be limited to that giving the desired tone, whether the ink lays or not. There is thus a chance to introduce a third ingredient, beside black and toner, whose function is to make the ink lay. This monox does very nearly perfectly.[3]

[1] Come off upon the back of the next sheet laid upon it.

[2] Inserting of intermediate protective sheets between those freshly printed.

[3] The frontispiece of this volume was made from an original flashlight photograph, and printed with "Monox Ink" from a cut which was flat-etched and run without overlay on a Colt-Armory press, running at 1,500 impressions an hour.

CERAMICS.

All ceramic materials contain silica, and are fired to render them permanent in form or location. Many of the technical difficulties are due to the firing. As monox may burn to silica under proper conditions of mixture with oxides or exposure to oxidizing flame, it may, in certain cases, be substituted for a part or all of the silica with advantage.

In burning to silica, monox liberates considerable heat, and thus a sort of auto-firing may occur. This seems to promise certain advantages in glazes and in other departments, but it is at present too early to definitely state.

LUBRICATION.

Monox is so fine that it was thought that it might have some lubricating value, like graphite, but this did not prove to be the case, as the friction of a bearing wet with oil containing monox is no less than when wet with oil alone. The only advantage, at first, seemed to be that a mixture of monox and machine oil gets thicker, instead of thinner, when heated, and is thus less likely to run away in time of trouble.

Later, a curious observation was made, namely, that after a bronze bearing has run with monox and oil for a time, it may then be washed clean and dry with gasoline and run under similar load for a considerable time without any lubricant at all and without heating. The limiting conditions of this action are not known at present, but it is supposed to be due to the particles of monox setting into the bearing metal and forming a vitreous surface. There are certainly some interesting possibilities suggested that warrant further study of this phenomenon.

Monox has been investigated somewhat as a polishing powder and as a heat insulator, with some success.

I wish, in conclusion, to give much credit to Mr. F. S. Hyde for his painstaking work in the making and testing of paints, and to Mr. J. M. Fitzgerald, expert painter, for his technical skill and criticism, to Mr. A. Cochard for much counsel regarding inks, and to Mr. E. Ward, expert printer, for his skill and his excellent judgment of quality in printing.

A paper read at the Twelfth General Meeting of the American Electrochemical Society, in New York City, October 19, 1907; President C. F. Burgess in the chair.

THE PRODUCTION OF "MONOX," A NEW ELECTRIC FURNACE PRODUCT.

By Henry Noel Potter.

In separate communications, the writer has referred to the product "monox," both from the standpoint of chemical theory and from that of industrial application. It remains to describe how this product is made and show that its manufacture is a practical commercial possibility.

Silicon monoxide is produced when silica, ordinarily in the form of glass-makers' sand, is heated in contact with coke, graphite, silicon carbide, silicon or intermediate reducing agents, such as siloxicon and carborundum fire-sand, containing silicon, carbon and oxygen.

Under the usual conditions of electric furnace arrangement and operation, the silicon monoxide cannot escape, and is further reduced to silicon or to silicon carbide. It exists under such conditions only transiently, but can be shown by inserting a carbon tube into a furnace which is producing silicon. Through this tube a brown smoke and gases may be drawn, representing the condensed atmosphere within the furnace. This will be found to contain silicon monoxide in abundance, but little or no free silicon. This appears to be due to the high boiling point of silicon, which lies higher than the sublimation temperature of silicon monoxide, so that on gaseous silicon monoxide being educed, liquid silicon results, which doubtless condenses into drops, trickles down the walls, and so collects in the pool where it is found.

The liberation of both silicon monoxide and carbon monoxide as gases causes an elevation of gas pressure at the reaction locus. If the thickness and weight of charge above the region of reaction is not great, and if there is a free space above the charge, the gases will work their way upward and outward with such force as to open a passage through the overlying charge, and

through this passage the hot gases will rush, widening it out into a throat and piling up a cone of displaced material about the throat opening, like a little volcano.

Under such conditions, there can be no great increase of gas pressure in the reaction region, and the gases, as soon as they form, burst out through the throat in an incandescent blast.

Thus, it happens that the silicon monoxide does not remain long enough in the reaction region to become fully reduced, but escapes almost as soon as formed, and is chilled, by radiation and otherwise, very rapidly.

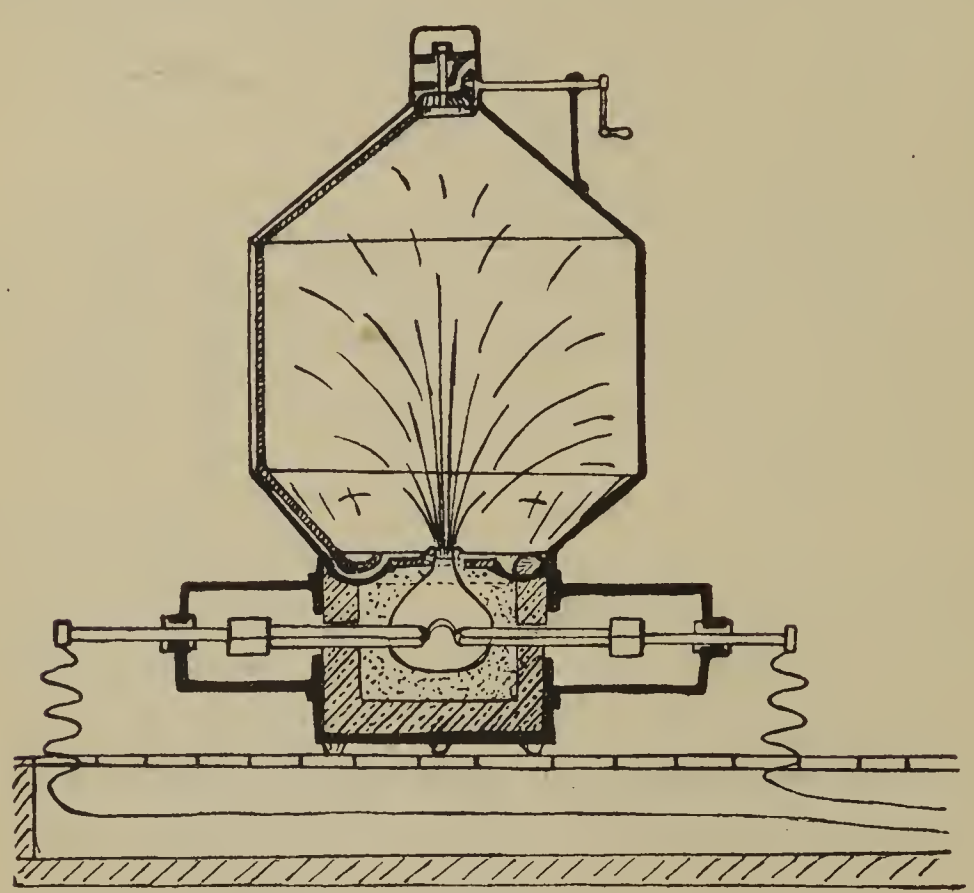


FIG. 1.

If such a throat discharges silicon monoxide and carbon monoxide into the air, they burn with great violence and liberation of heat, with production of clouds of fine silica.

If, on the contrary, the throat discharges into a large container free from air, preferably under reduced pressure, the products in the blast do not burn, but cool with great rapidity and deposit on the walls and all exposed surfaces within the container the fine brown powder which is termed "monox."

The present furnace is the latest of a number of experimental devices, and consists of a cylindrical cast-iron drum about 4 feet in diameter, lined with a 7-inch wall of firebrick. Diametrically

opposite each other, and bolted to the drum, are cast-iron terminal boxes, within which are located electrode clamps and a screw and nut mechanism for moving the electrodes back and forth. This mechanism and the clamps are mounted in insulating supports, and motion is effected by insulated shafts entering the terminal boxes through stuffing boxes. Electrical connection is maintained through two massive copper tubes, which slide through the rear walls of the two terminal boxes, through insulated stuffing boxes.

The terminal boxes have doors, provided with rubber gaskets in the form of tubes, through which water, under pressure, circulates, in service insuring a gas-tight joint and keeping the gasket and adjacent metal surfaces cool at the same time. These water-cooled expansion gaskets are used in a number of places about the furnace, and contribute in no small degree to its success, as they do away entirely with bolts, nuts and washers, asbestos gaskets, and all the time-wasting details of what may be termed standard practice. The doors are shut and the water turned on, and this is all there is to making a gas-tight fit. When the doors need to be opened, the pressure is equalized inside and out, the water turned off, and the door opens without any difficulty. The copper tube forming the electrical connection to the electrode is water-cooled, the water entering through a small tube in the bore of the large one, thence out around the small tube. The electrode clamps are also water-cooled, as otherwise the bolts and nuts get so hot as to stretch and jam. It is the best practice to water-cool all parts where any mechanical action occurs. The electrodes themselves are 4-inch square bars of either Acheson graphite or carbon. These are horizontal, and meet in the center of the large brick-lined drum.

The top of the drum is open, and a balloon cover fits upon it, with a water-cooled expansion gasket to make it tight. The cover is a boiler-plate cylinder, 7 feet in diameter, with a conical top and a conical reduction where it joins the drum.

Within the cover are scrapers, which hang from a central spider in the top of the cover, and are driven by gears operated by a shaft entering through a stuffing box. The cover is cooled by a film of water which trickles down over its outer surface and

is caught in a gutter below. It does not heat up very rapidly, and a little water serves to keep it cool enough.

The charge consists of a mixture of sand and coke, or sand and carborundum fire-sand, to which a little coke is added to increase the yield.

The drum is entirely filled with charge to a height of 12 inches

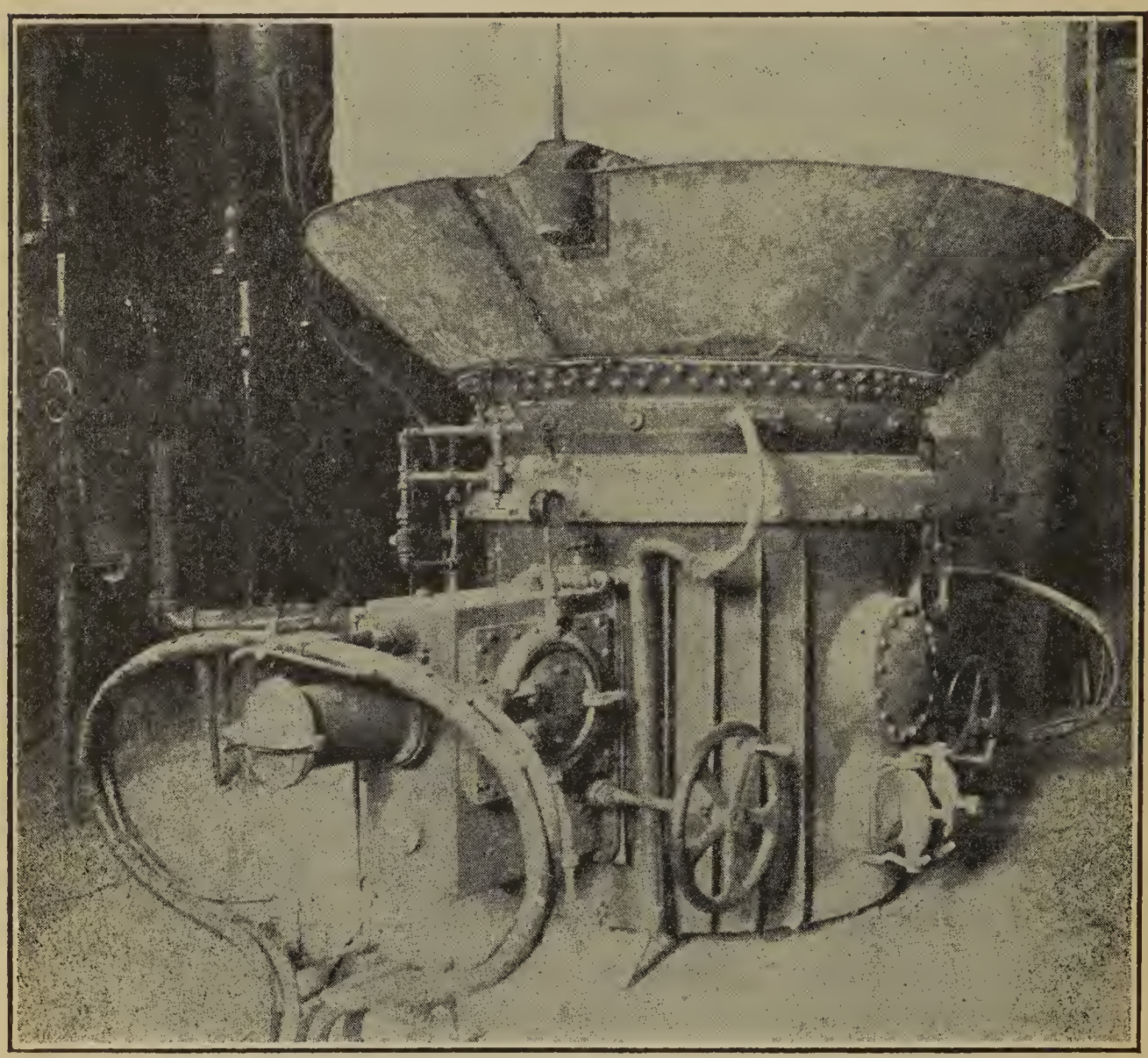


Fig. 2.

or more above the electrodes. The top of the charge is then weighted down with fire-brick, and directly above the arc a graphite ring, with a 7-inch opening in its center, is laid on the charge and a part of the charge dug away through the ring to make a weak place in the charge, so that the reaction gases shall blow out through the ring, and thus build the throat in the axis of the furnace.

Once the furnace is charged and has been operated, it can be

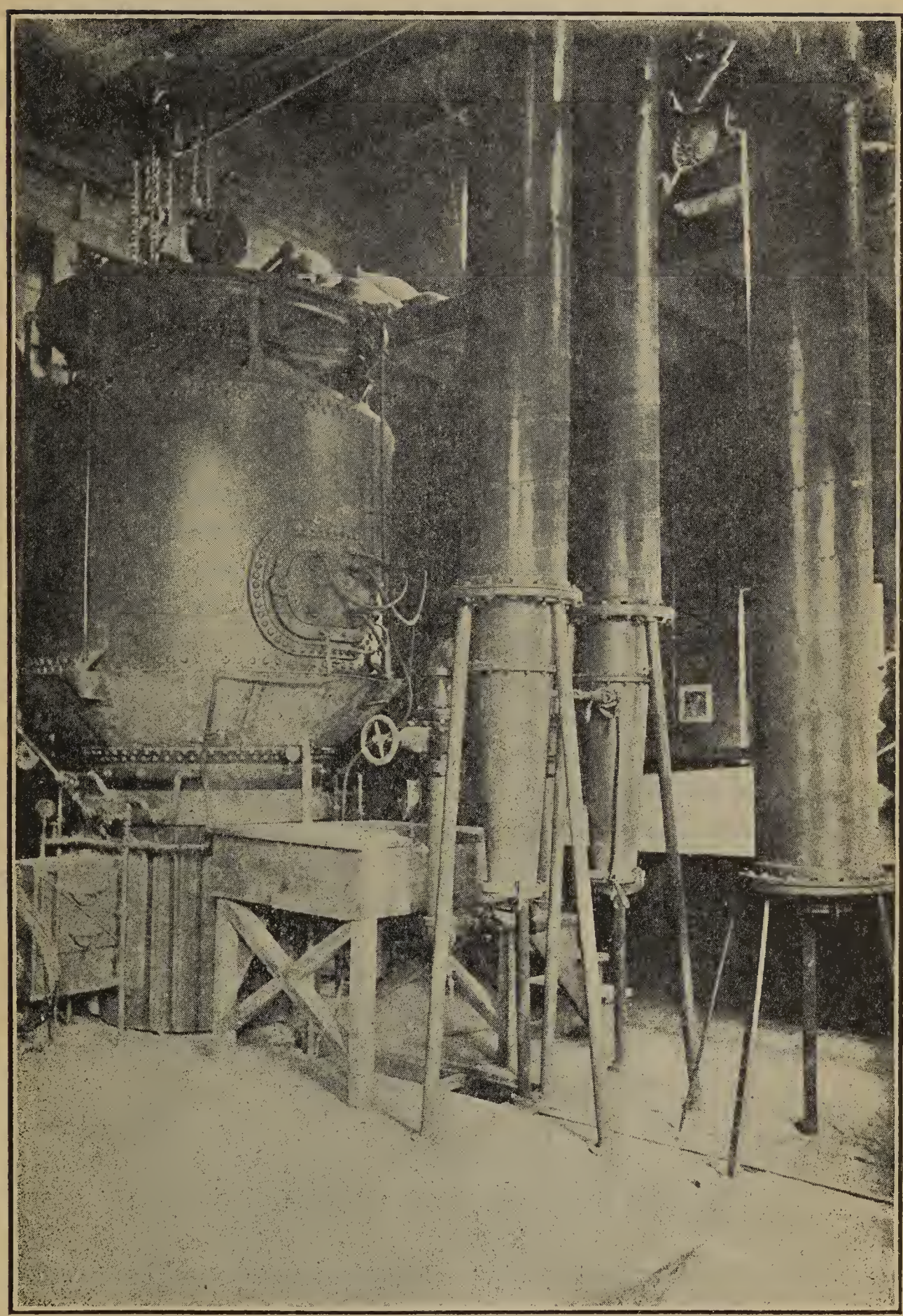


FIG. 3.

recharged by pouring fresh charge down the open throat, and only when an electrode breaks or has to be renewed is it necessary to dig out the furnace. Even this can with care be done away with, and all the exigencies of service met without disturbing the great body of material inside the fire-brick lining.

The electrical equipment consists of a special rotary field alternator, designed to operate a single arc of the full capacity of the machine at or near the top of the volt-ampere characteristic curve of the dynamo. It is separately excited, and can be open-circuited or dead-short circuited without injury to itself and without stalling the gas engine driving it.

This generator was designed by Mr. Tingley, of the Westinghouse Electric and Mfg. Co., particularly for this service, and it may be regarded as the first of an intermediate type of dynamo between the constant potential and constant current types. This may be appropriately termed the electric furnace type, as its peculiar virtue is to maintain an arc without any necessary regulation external to the armature.

I wish to give great credit to Mr. Ames S. Albro, engineer in charge of the large arc furnace, for his great resourcefulness in avoiding and overcoming the many difficulties which surround all work with experimental apparatus; to Mr. Herman Siegel, who has operated all the "monox" furnaces, from the smallest to the present, with most gratifying skill; and to every one who, each in his way, has contributed his best with willingness and enthusiasm to this development.

A paper read at the Twelfth General Meeting of the American Electrochemical Society, in New York City, October 18, 1907; President C. F. Burgess in the chair.

ANALYSIS OF SILICON COMPOUNDS.

By A. Bliss Albro.

The method herein described was devised by the author for analyzing silicon, silicon monoxide and ferro-silicon as made by processes invented by Dr. Henry Noel Potter, and was developed and improved in connection with this work. In its present state it has been in use for a number of years and has proven thoroughly reliable.

The method of analysis which involves fusion with sodium or potassium compounds is, in general, to be avoided, owing to the fact that some of the sample is liable to be lost in case the fusion is stirred to secure complete mixture. When such stirring is not done and the dish is covered until a state of quiet fusion is reached, some of the sample is thrown on the sides of the dish and is not acted on. These general objections apply to all sodium and potassium compounds, but in the case of sodium peroxide, which is quite generally used in the analysis of silicon at present, several objections of a more serious nature present themselves and are stated below.

While sodium peroxide may be used for analyzing low-grade ferro-silicons with the proper precautions, it cannot be used with high-grade ferro-silicons, silicon nor silicon monoxide with safety to the operator nor with accuracy. This is owing to the fact that a mixture of sodium peroxide and finely pulverized silicon, silicon monoxide or even 50 per cent. ferro-silicon is spontaneously combustible unless kept in an absolutely dry atmosphere. The slight friction due to mixing the two together in the air is sufficient to start an extremely rapid and violent reaction between the silicon or its compounds and the peroxide. The rapidity of the reaction may be reduced to any desired point by the addition of varying amounts of some inert material—preferably finely-pulverized silica—and correcting for this in the analysis. This, however, entails additional work which should be

avoided as far as possible, and also requires that the silica should not only be of known purity, but that the kind and percentage of impurities should also be known. The peroxide also introduces impurities.

A further objection to the use of sodium peroxide is met with when analyzing silicon containing silicon carbide, as the latter is dissociated by the peroxide with the liberation of carbon dioxide. Even when the liberated gas is absorbed by a special apparatus this analysis shows the following possible errors: First, the peroxide almost invariably contains or absorbs carbon dioxide, which it liberates, and thus introduces either an error or a correction factor; second, if there is any free carbon present in the sample no distinction can be made between it and the carbon from the carbide without a separate analysis; third, and most important of all, the silicon from the carbide passes into the fusion the same as the free silicon and is credited as existing in the elemental state.

In cases which have come under the writer's observation it is evident that this method has been used and the carbon analysis made by collecting the carbon dioxide evolved by such fusion, crediting the absorbed gas to free carbon alone, which, on the face of it, is incorrect. Analyses have been observed stating that the silicon contained as high as 4.5 per cent. of free carbon. The error of this is evident from the fact, as discovered by Dr. Potter, that silicon may be melted in contact with carbon without any free or combined carbon being found in the silicon or any free or combined silicon in the carbon, and it is therefore evident, without going into the details of the reaction temperatures, that free carbon to the amount of even 1 per cent. is, I believe, impossible unless the material includes it mechanically in its mass. As an example of the error introduced by the method of analysis under discussion, take a sample of silicon which actually analyses —72.00 per cent. Si, 20.00 per cent. SiC, 0.75 per cent. C, 0.75 per cent. Fe, 0.50 per cent. Al, 0.40 per cent Ca and 0.60 per cent. Mg. This material would show the following comparative analyses:

	Actual Analysis.	Sodium Peroxide Analysis.
Si	72.00 per cent.	89.57 per cent.
SiC	25.00 " "	00.00 " "
Free C	0.75 " "	8.18 " "
Fe	0.75 " "	0.75 " "
Al	0.50 " "	0.50 " "
Ca	0.40 " "	0.40 " "
Mg	0.60 " "	0.60 " "
	100.00 " "	100.00 " "

Analyses showing discrepancies as great as the above have come under the writer's observation.

It therefore became evident that some method of analysis was necessary which would be comparatively rapid, of a high degree of accuracy, distinguish between free and combined carbon without any extra analyses on fresh samples, introduce no impurities in the reagents used, and finally, something impossible by any fusion method, give the percentage of silica present in the sample analyzed.

It is thought that the following method fulfills all the above requirements, is open to objection at fewer points than any method yet published, and is not complex in manipulative details. The novelty of the method consists in the materials used, the methods of manipulation and the combination of the various single determinations.

To secure a representative analysis of silicon or ferro-silicon, care must be taken in securing the sample. Pieces should be broken from the various portions of the interior of the mass, carefully avoiding the nodules extruded on the top surface while cooling, as these are much purer than the main body of the material, and, being relatively small in amount, are not representative samples. In analyzing a large quantity of silicon, at least 20 grams of small pieces should be secured. These are then ground to pass 100-mesh sieve, and the whole amount thoroughly mixed on a piece of glazed paper. The sample is then separated into 10 piles of approximately the same amount each, and each individual pile thoroughly mixed. Approximately, half of each pile is then transferred to a second piece of glazed paper, the whole thoroughly mixed, again separated into 10 piles and

each of these mixed as before. Then, with a platinum spoon, having approximately a capacity of 0.25 gram of silicon, equal samples are taken from each of the 10 piles, in this way securing a total sample of about 2.5 grams of the material. This sample is thoroughly mixed on glazed paper, and from it the duplicate samples are taken for analysis. The remaining material from the original 20 grams is transferred to a glass-stoppered bottle and reserved for confirmatory tests. It has been the writer's practice to use 1.2 grams for one sample and 0.9 grams for the other in duplicate analyses, weighing the two on thin platinum foil or in a light-weight platinum dish.

The sample is washed into a silver dish of about 250 c.c. capacity with warm distilled water. In a second silver dish of about 100 c.c. capacity, dissolve 7.5 grains of c. p. sodium hydroxide (or potassium hydroxide) in 75 c.c. of distilled water. Place the two dishes containing the sample and the caustic solution on an asbestos plate over a low flame and bring both to boiling. Remove the flame from under the sample and slowly pour the caustic solution upon it, stirring with a silver rod. A rapid reaction ensues, and the dish should be almost completely covered with a silver plate during this operation and tightly covered after the addition of the caustic until the reaction has ceased. This will require about two minutes. The cover is then removed, any adhering material being washed from it into the dish and 100 c.c. of boiling distilled water added. (See remarks for treatment when analyzing silicon monoxide.)

In the meantime, a hardened filter paper should be dried in an air bath at 125° C. for one hour, transferred to an air-tight glass container of light weight, and weighed, after cooling the container and paper in a desiccator. As the same container is used for reweighing the paper and any precipitate later, the weight of the container need not be known.

The contents of the silver dish are filtered through this paper, using a hard glass funnel, as it has been determined that the dilute caustic solution will not measureably attack such a funnel during filtration.

Silver funnels may be used if desired, but are not necessary. The filtrate (called filtrate A) is caught in a 400 c.c. platinum dish containing 35 c.c. of concentrated c. p. hydrochloric acid.

After the filtrate has passed through the paper the precipitate, if any (called precipitate "A"), is washed twice with boiling distilled water, once with about 5 c.c. of conc. hydrochloric acid added drop by drop along the top edges of the filter paper (except in the case of ferro-silicon, when it is washed with the acid until all precipitated iron hydroxide is dissolved), and then with boiling distilled water until five drops of the wash water produce no turbidity in a solution of silver nitrate. The last washing can well be done with the aid of a filter pump, as hardened filter paper is used for this purpose. It has been found that the total volume of Filtrate "A" including washings should be about 300 c.c.

The platinum dish and contents are placed on an asbestos plate over a strong flame and 20 grams c. p. sodium chloride are added (or potassium chloride if potassium hydroxide was used). The addition of this amount of chloride has been found to be the amount necessary to start a crystallization of salt from the solution at the concentration where bumping is liable to begin, due to the separation of silicic acid. No bumping takes place if salt crystals begin to form at or before this separation, and the evaporation of the solution can be carried on much more rapidly without this danger of loss.

A platinum dish must be used, as it was found that the best porcelain loses its glaze in two evaporations and that unglazed porcelain loses measurably in weight in one evaporation.

When visible water begins to disappear the flame is turned very low and the process continued until no vapors are given off, stirring the dry mass frequently with a platinum spatula to break it up into a fine powder.

When dryness is reached, remove the flame entirely, allow dish and contents to cool to the temperature of the hand, add 20 c.c. of conc. c. p. hydrochloric acid, stir until the whole mass is thoroughly moistened, replace flame and evaporate to dryness a second time. Allow the dish to cool as before, and add the same amount of acid, evaporate again to absolute dryness and allow the dish to cool to room temperature. Then wash down the sides of the dish with 50 c.c. of conc. c. p. hydrochloric acid. Stir the whole mass together and allow to stand at room temperature for 20 to 30 minutes.

While filtrate "A" is evaporating, precipitate "A" should be treated as follows: The filter paper, contents, and glass container are dried separately for one hour at 125° C. in an air bath, the paper and contents placed in the container, cooled in a desiccator and weighed. The difference between this and the first weight of the paper and container is the total amount of material insoluble in a 1 : 10 caustic solution. The filter paper and contents are then transferred to a weighed platinum dish, incinerated and weighed; the loss in weight after correcting for filter paper ash is a measure of the free carbon present in the sample. The contents of the platinum dish is then treated with conc. c. p. hydrofluoric acid and a few drops of conc. c. p. sulphuric acid, evaporated to dryness, retreated with acids, ignited and reweighed—the loss in weight being the measure of the silica caught on the filter. The residue in the platinum dish is then treated with mixed hydrofluoric and nitric acids, heated, allowed to stand ten minutes, diluted and filtered, catching the filtrate (called filtrate "B") in a 100 c.c. platinum dish. The material on the filter is washed thoroughly and the washings added to filtrate "B." The filter paper and contents are incinerated and weighed, the corrected weight being that of the silicon carbide present in the sample, unless there is reason to suspect the presence of other substances insoluble in the mixed nitric and hydrofluoric acids.

Filtrate "B" is evaporated to dryness, treated with a few drops of conc. c. p. sulphuric acid and again evaporated to dryness. The residue is then taken up with conc. c. p. sulphuric acid, to which is added a little hydrochloric acid and water, and the whole boiled until the solution is clear. This is then added to filtrate "D," to be described later.

After the hydrochloric acid has been allowed to act on the evaporated filtrate "A" for twenty minutes or more, the contents of the dish are washed into a 600 c.c. glass beaker, diluted to 350-375 c.c. and heated to about 85° C. The silica is thus freed from the chlorides which are filtered off through close-fibered filter paper, the filtrate (called filtrate "C") being caught in the platinum dish. The precipitated silica (called precipitate "C") is washed on the filter once with boiling distilled water, once with conc. c. p. hydrochloric acid, and then with boiling distilled water until free from all chlorides.

Filtrate "C" and the washings are then evaporated to dryness in the platinum dish as before, treated once with 20 c.c. of conc. c. p. hydrochloric and evaporated to dryness. The dried material is allowed to stand until it cools to room temperature, when 50 c.c. of conc. c. p. hydrochloric are added and allowed to act on the residue for twenty to thirty minutes. The contents of the dish are then washed into a 600 c.c. beaker and diluted to about 350 c.c., heated to about 85° C. and filtered, catching the filtrate (called filtrate "D") in a beaker of about 800 c.c. capacity. The precipitate will in this case be very small, but is treated on the filter paper the same as precipitate "C," *i. e.,* washed once with boiling distilled water, once with conc. c. p. hydrochloric acid, and then boiling distilled water until free from all chlorides, the washings all being added to filtrate "D."

Precipitates "C" and "D" contain the silica from the silicon of the sample and some iron and aluminum oxides held within the particles of silica. By the treatment herein given it has been found that less than 0.05 per cent. of the silica will be found in filtrate "D," and this can be recovered by a third evaporation where such accuracy is desired. The precipitates "C" and "D" are transferred to a weighed platinum dish while still moist and incinerated over a low flame until all carbon from the filter paper has been consumed, when the dish and contents are heated over a blast flame or triple Bunsen burner for at least fifteen minutes, after which time the dish is transferred to a desiccator, allowed to cool for at least thirty minutes and weighed.

The silica thus obtained is impure, and to determine its true weight the impure material is moistened with water and treated with conc. c. p. hydrofluoric acid and a few drops of conc. c. p. sulphuric acid, evaporated to dryness, retreated with the acids, re-evaporated, ignited and weighed—the loss in weight being taken as the true measure of the silica. The process should be repeated until a constant weight is secured. After weighing, the residue is treated with a few drops of conc. c. p. sulphuric acid and a few drops of conc. c. p. hydrochloric acid, boiled and evaporated to dryness, retreated with the mixed acids, boiled, diluted with a few c.c. of distilled water and boiled until a clear solution is obtained, which is then added to filtrate "D," together with filtrate "B."

Filtrate "D" is then boiled and three grams of c. p. ammonium chloride, and ammonia in excess added to it, boiled for five minutes, and filtered, the filtrate (called filtrate "E") being caught in a beaker of about one liter capacity. The precipitate (called precipitate "E") contains the iron and aluminum as hydroxides, and is washed on the filter paper with boiling water containing 1 per cent. of c. p. ammonium nitrate until free from chlorides, adding the washings to the filtrate.

Precipitate "E" is then transferred while moist to a weighed platinum dish, igniting the paper and precipitate separately, and when all carbon from the filter paper has been consumed the residue is treated with a few drops of conc. c. p. nitric acid and again ignited to a dull red, when it is cooled in a desiccator and weighed as $Al_2O_3 + Fe_2O_3$. In the case of silicon, when it is desired to know the amount of Fe and Al, and not the combined weights, this residue is treated with a mixture of conc. c. p. hydrochloric and sulphuric acids, diluted and boiled to a clear solution and then evaporated until copious fumes of sulphuric acid are given off, when it is allowed to cool, diluted with distilled water, reduced with c. p. zinc and, after dilution to the required amount in accordance with the assumed weight of Fe_2O_3 present, titrated with N/20 permanganate solution. The aluminum is determined by difference and the iron calculated as $FeSi_2$, correcting the silica found in precipitates "C" and "D" for the Si contained in the $FeSi_2$.

In the case of the ferro-silicons, the iron content being large, some platinum chloride is formed in filtrate "D" owing to the evaporation of the iron chloride solution in contact with the platinum. This is readily removed by boiling the solution, saturating with hydrogen sulphide and filtering off the platinum sulphide and free sulphur. The filtrate is then boiled to expel all H_2S and the iron oxidized back to the ferric state by the addition of a slight excess of bromine water, which excess is expelled in turn by boiling. The mixed hydroxides are then precipitated and treated as hereinbefore stated.

Filtrate "E" contains the calcium and magnesium and is evaporated to one-third its bulk, boiled, and the calcium precipitated from the boiling solution by the addition of a boiling solution of ammonium oxalate; then the boiling is continued for

ten or fifteen minutes and the solution set aside for a few hours. The calcium oxalate is then filtered off, ignited wet in a platinum dish, finally heated over a blast lamp for twenty minutes, and weighed as calcium oxide.

The filtrate from the calcium oxalate precipitation is evaporated to dryness and gently ignited to expel all ammonia salts, after which it is treated with hydrochloric acid and water, filtered, and the magnesium precipitated in accordance with the method of W. Gibbs or that of H. Neubauer. The precipitated phosphate should be washed with a 2.5 per cent. ammonia solution and dried in the air bath before incineration. The incineration should be carried on over a low flame until all ammonia has been driven off, and then the flame should be gradually increased to its greatest intensity. The precipitate is calculated to magnesium.

The aluminum, calcium and magnesium are calculated as existing in silicon and its compounds in the elemental state in this analysis, but to make it absolutely accurate they should probably be calculated as silicides. However, for commercial purposes, the silicon of these silicides is practically as available for reduction purposes as free silicon, which is not the case with carbon silicide (silicon carbide). The silicon of the $FeSi_2$, the form in which iron is present in ferro-silicons made in the electric furnace,[1] is equally available with the silicon of the silicides mentioned above, but as the iron is calculated as $FeSi_2$ in the ferro-silicons, the same practice is adhered to in analyzing silicon.

REMARKS.

When analyzing silicon monoxide, the dilute caustic solution should be allowed to act only so long as hydrogen is evolved, the contents of the dish then being poured over ice in a platinum dish surrounded by a freezing mixture. The action of the caustic ceases at once, and in this way errors due to dissolving silica are greatly reduced—it being found that a 1 : 10 boiling caustic solution in one hour dissolved only about 1 per cent. of amorphous silica fine enough to pass 300-mesh bolting silk, the concentration of the caustic solution being kept practically constant by the addition of water every five minutes during this

[1] Microstructure of Silicon and Alloys Containing Silicon, A. B. Albro. Trans. A. E. S., Vol. VII, 1905.

time. The solubility of crystalline silica in dilute caustic solution is very much less.

It is well to bear in mind the fact, as stated by Dr. Potter in his paper on "Silicon Monoxide,"[2] that silicon, ferro-silicon and silicon carbide become rapidly coated with an oxide film, thus changing their apparent properties. For example, silicon carbide may be completely destroyed by repeated treatments with hydrofluoric acid, when it is exposed to the air between treatments, and thus allowed to coat itself with an oxide film.

As iron, aluminum, calcium and magnesium constitute the main metallic impurities found in silicon and ferro-silicon, these are the only ones discussed in this analysis, however, occasionally, chromium, maganese and titanium will be found in the ferro-silicon if the furnaces have been recently used for making ferro-alloys of these elements. Qualitative tests should be made if the presence of these elements is suspected, which, if positive in their results, should be followed by a quantitative determination which can be interspersed in the analysis given above.

A check on the impurities contained in the silicon, silicon monoxide or ferro-silicon may be rapidly made by the following analysis, which has been termed by the writer "Rapid Analysis of Silicon Compounds":

After proper sampling and weighing, as outlined in the first part of this paper, the weighing being done in a platinum dish of about 75 c.c. capacity, the sample is moistened with distilled water and then treated with a mixture of about 30 c.c. of concentrated c. p. hydrofluoric acid and 10 c.c. of conc. c. p. nitric acid. The hydrofluoric acid is added first and then the nitric acid is added drop by drop, owing to the violence of the reaction. After all reaction has ceased, the solution is diluted and filtered through a weighed hardened filter paper. This is dried and weighed the same as precipitate "A" in main analysis, the gain in weight being a true measure of the free carbon and silicon carbide in the sample. It is then incinerated, the loss in weight after correcting for filter paper ash being free carbon and the residue silicon carbide.

The filtrate is caught in a platinum dish, evaporated to dryness, treated with a few drops of sulphuric acid, re-evaporated, taken

[2] Trans. A. E. S., Vol. XII, 1907.

up with sulphuric acid, to which a small amount of hydrochloric acid is added, heated to boiling, diluted with distilled water, boiled until a clear solution is obtained, evaporated until copious fumes of sulphuric acid are given off, diluted with distilled water and treated the same as filtrate "D" in the complete analysis; *i. e.*, the iron, aluminum, calcium and magnesium determined. The silicon is calculated by difference.

This analysis has been proved to be accurate to within 0.3 to 0.4 per cent. of the total silicon content of commercial silicon and silicon compounds, as compared with the results obtained by the longer method. This method is especially useful in analyzing ferro-silicon containing less than 75 per cent. of silicon. The results always show slightly higher silicon values than actually exist, owing to the fact that all the material volatilized by the mixed acids appears as silicon in the final result.

A paper read by title at the Twelfth General Meeting of the American Electrochemical Society at New York City, October 18, 1907.

ELECTROCHEMICAL METHODS FOR THE QUALITATIVE AND QUANTITATIVE DETERMINATION OF FREE SILICON IN THE PRESENCE OF SILICA, SILICATES, OXIDES, FREE CARBON AND SILICON CARBIDE.

By William Roy Mott.

For analyzing the many electric furnace products that are being produced, the writer has seen no method recorded for accurately determining small amounts of free silicon in the presence of silica, silicates, metallic oxides, free carbon and silicon carbide. There is the well-known *indirect* method of oxidizing the silicon to silica, and from the gain in weight, due to oxidation, calculating the free silicon, if there be no other reaction. But the free carbon is also easily oxidized, as well as small amounts of silicon carbide. Even when the free and combined carbon is known—both before and after treatment which oxidizes the free silicon—the corrected result still is uncertain, especially where the actual amount of free silicon is relatively small. These difficulties are overcome by some electrochemical methods which the writer worked out over three years ago, and these methods may be of interest and value to workers on electric furnace products.

One of these furnace products of great value is silicon carbide, which is a very hard, brittle, crystalline substance that, when very pure, is colorless and semi-transparent. The bright colors, observed on silicon carbide, are not due to iron or other impurities, but rather to a very thin (0.00001 to 0.0001 centimeter thick), colorless layer of silica, which produces the same play of colors as is observed on an oil film on water. This conclusion is verified by treating silicon carbide crystals with hydrofluoric acid, which dissolves the iridescent layer of silica, leaving the silicon carbide crystals a dull, uniform gray. This layer of silica is an

important factor in the analysis of the products of electric furnaces.

Chemically, silicon carbide is one of the most inert substances, resisting nearly all aqueous solutions.

Silicon was a rare metal until F. J. Tone, a few years ago, succeeded in producing it in large quantities. Since then, its commercial importance and number of valuable uses have been continually increasing. Metallic silicon is not acted upon by pure nitric acid or by pure hydrofluoric acid, but it is readily dissolved by a mixture of nitric acd and hydrofluoric acid. In general, silicon is soluble in hydrofluoric acid by aid of an oxidizing agent. Nitric acid, ferric salt and dissolved air are examples of such oxidizing agents which react on free silicon in hydrofluoric acid solutions.

Silicon, like aluminum, is soluble in alkali with evolution of hydrogen. This hydrogen gas might be collected and used as a measure of the free silicon. This is, however, not satisfactory, as it requires special apparatus and good manipulation; and further, the reaction is so slow as to lead to loss of hydrogen, because traces of oxidizing agents are thus given time to act appreciably. Silicon that is dissolved by caustic can be determined as silica, but the result is too high, owing to the slight amount of silica that is also dissolved. This error can be corrected. If there is no third reaction, then the gain in weight of *all the solid matter* is due to the oxygen combined with the free silicon, which can then be calculated. This method is the most satisfactory of the chemical methods for determining free silicon. For small amounts of free silicon this chemical method is not as good as the electrochemical methods, but it is slightly better for determining large amounts of free silicon.

Silicon dissolved by fusion is oxidized to silica, but as carborundum is also oxidized to silica, more difficulty is experienced in analysis for free silicon than by solution in caustic. Also, in fusion methods great risk is taken with the platinum crucible. At dull, red heat, small specks of silicon will fuse with the platinum, making capillary pores in the bottom of the crucible, which ruin both the analytical results and the crucible.

Another chemical method is to take ferric salt in solution and determine the amount reduced by the material containing silicon.

Several tests showed this method to give results of little or no value. The reason will appear evident in the following discussion of the electrochemical methods for determining free silicon.

When iron is placed in a solution of copper sulphate, the iron goes into solution and the copper is deposited. This reaction is the result of many local galvanic circuits, where the iron is dissolved and the copper is deposited by the local current. When silicon is placed in a solution of copper sulphate there is no reaction, because the silicon is protected by a very thin layer of silica; but, on adding hydrofluoric acid, this protecting layer of silica is destroyed and the copper is precipitated by the silicon in a manner exactly analogous to the well-known replacement of copper by iron when it is placed in a copper solution. As copper is a metal with very distinct color, it is better for qualitative purposes than other metals that might be used. The color appears in a few minutes on material containing free silicon when this is put into a solution of copper sulphate containing hydrofluoric acid. Of course, the more concentrated the solution, the better is the test. It is especially convenient, as it requires only two chemicals which are generally available in most laboratories and a dish suitable for resisting hydrofluoric acid.[1] A platinum, silver, copper, paraffined glass, or wax basin can be used for the test. For qualitative purposes, the solution of copper sulphate and hydrofluoric acid needs to be kept in contact with the silicon-containing material for only a few minutes; but for quantitative results a much longer treatment is required. Since copper is redissolved slowly by hydrofluoric acid in the presence of air, the method is not so accurate as one using a metal insoluble in the presence of air. Such a metal is silver, and it proved satisfactory for quantitative work.

Silver nitrate could not be used, as the nitric radical would also react with silicon in the presence of hydrofluoric acid. So the formation of a pure solution of silver fluoride with hydrofluoric acid is advisable. The commercial product called silver oxide is unsatisfactory for use in preparing silver fluoride solution. It is advisable to prepare the silver fluoride solution as follows: Take pure silver nitrate, precipitate with excess of potassium hydroxide, and filter and wash the precipitate several

[1] Caution: All hydrofluoric acid solutions should be handled with the greatest care, as they easily cause sores lasting months.

times with distilled water until all nitrate is washed out. Then carefully remove the precipitated silver compound from the filter and treat in a suitable vessel with an excess of chemically pure hydrofluoric acid, which forms a solution of silver fluoride in excess of hydrofluoric acid. This solution of silver fluoride is used on the material containing silicon.

The material to be analyzed can be ground in an agate mortar, which will be partially abraded, as silicon carbide is the harder material, but this, however, does not interfere with the accuracy of the result as it does where chemical methods for determining free silicon are used. To determine the total free silicon in the material it is only necessary to grind fine enough to pass sieve No. 150.

The treatment with silver fluoride solution should be made in a platinum dish and continued from one hour to a day. About 30 cubic centimeters of solution is sufficient for a determination where the silicon is in relatively small amount, but silver in solution should be more than equivalent to all the free silicon. It is convenient to have the determination use up about half a gram of metallic silver. The residue containing the deposit of silver is washed free from the silver fluoride solution with distilled water until tests with a soluble chloride solution give no trace of a silver chloride precipitate in the wash water. The metallic silver is deposited very rapidly and grows out in fungi-like growths of porous metal.[2] The silver is carefully dissolved by dilute nitric acid alone, filtered and treated in the regular way to precipitate the silver as silver chloride, which is weighed after taking the usual precautions. Or the silver may be determined by one of the several volumetric methods. Also the silver in solution may be determined in a metallic form by electrodeposition on a cathode.

The reaction of silicon in electrochemically precipitating metallic silver is as follows: $Si + 4\ AgF = 4\ Ag + SiF_4$. As silicon is tetravalent and silver is monovalent, one atom of

[2] At this point we can complete the determination for most practical purposes by weighing the washed and dried residue containing the metallic silver and then by weighing the insoluble residue which is left after treating with nitric acid. Since this residue has been previously treated with hydrofluoric acid there is ordinarily relatively slight action upon it by the pure nitric acid. If there is no other reaction then the loss in weight of the residue corresponds to the metallic silver. Of course, in the calculations we use the silver ratio of one to 15.20. This short-cut method has not been found to have quite the accuracy of the method where the silver chloride is the basis of the analysis.

silicon replaces four atoms of silver, forming four molecules of silver chloride. 28.4 grams of silicon would deposit $107.9 \times 4 = 431.6$ grams of metallic silver which would form $(107.9 + 35.5) \times 4 = 573.6$ grams of silver chloride. One gram of silicon would deposit 15.20 grams of metallic silver, which would form 20.20 grams of silver chloride. Thus one milligram of silicon would be multiplied in effect on the balance by 20.20 times. This is an unusually large ratio and is of advantage when small amounts of silicon are to be detected. The writer has made quantitative determinations where the free silicon formed only about one-millionth part of the material analyzed.

It is quite surprising how completely the silicon is replaced by the silver, and a third treatment of the residue is necessary only where great accuracy is desired. When analyzing a substance that is nearly all silicon a third treatment is advisable. The accuracy of the results can be brought within 1 per cent. of the total silicon.

To go beyond the limits of our title, we shall briefly consider what necessary steps should be taken where free metals are present. If the metals are such as replace silver it is evident that their amount must be determined and their stage of oxidation in the solution. This done, we can subtract the silver they would precipitate from the amount found and thus obtain the silver precipitated by the silicon. If the metals are in the form of carbides, then each special case requires new investigation, as some carbides readily react, while others do not. I know of no general rule for guidance. Silicon carbide has no reducing action on silver fluoride, but calcium carbide has reducing action. While thus stating the limitations of this method, it should be said that the method, so far as we know, would not differentiate between sub-compounds of silicon—such as the probable monoxide and a corresponding mixture of silicon and silica. When the amount of silicon is very great, the method is most serviceable in giving a limit below which we are certain there is at least the calculated amount of free silicon after the above corrections have been made. These corrections are often very small.

SUMMARY.

A direct process for determining free silicon consists in the treatment of the material to be analyzed with metallic fluorides,

such as copper fluoride, silver fluoride, etc. In one step the solid metallic silicon electrochemically replaces the metal in solution, which metal is deposited and may then be weighed or may be dissolved and determined in any regular way. These methods are direct and are not interfered with by the presence of silica, silicates, metallic oxides, free carbon or silicon carbide.

A paper read by title at the Twelfth General Meeting of the American Electrochemical Society at New York City, October 18, 1907.

ELECTROSCOPIC DETERMINATION OF THE RADIUM PRESENT IN SOME "TUFA" DEPOSITS FROM HOT SPRINGS, ARK.

By Herman Schlundt.

The Hot Springs of Arkansas are situated in the central part of the State, on the western slope of a ridge known as Hot Springs Mountain. The thermal waters issue from 50 separate vents in the old and gray hot-spring deposit, or "tufa," that covers the lower slopes of the mountain of sandstone and shale.[1] The total flow is estimated at 850,000 gallons per day. The thermal waters at Hot Springs correspond closely to the ordinary springs of the surrounding mountain region, save in the one characteristic of temperature. They are regarded as entirely normal springs whose waters have been heated in the course of their underground flow by steam rising through fissures in the rock, the source of the heat being a hot, igneous mass of intrusive rock underlying this portion of the State.

In 1904, Dr. Boltwood, at the direction of the secretary of the interior, made a thorough examination of the waters of these springs for radioactive properties.[2] In addition, samples of gases from two of the springs were examined; the residues from two samples of water were tested, and a sample of a spring deposit of "tufa" was included in the investigation. He tested all of the waters for radioactive gases—radium emanation—and a few of them for dissolved radium salts. Two water residues and one tufa deposit were tested for radium. The results of Dr. Boltwood's investigation showed that the waters possessed

[1] Weed, W. H., "Geological Sketch of the Hot Springs District, Arkansas." Senate Documents, Vol. 20, No. *282*, 79 (1902). (Government Printing Office, Washington, D. C.)

[2] The results are summarized in a paper published by Dr. Boltwood in the American Journal of Science, 20, 128 (1905).

radioactivity, the activity being due to the presence of radium emanation. Two cold springs on the reservation were tested and also found relatively high in activity. No indication of radium salts in solution was obtained. The deposit of tufa examined was found practically free from radium; Dr. Boltwood states that the quantity of radium present in the tufa was less than one-millionth of the quantity of radium associated with an equal weight of uranium in pitchblende, or, in other words, the radium content of the tufa has the same order of magnitude as that found in an ordinary soil sample. One of the points of special interest that the results of Dr. Boltwood's investigation presented was the existence of marked variations in the activity of the different water samples, whose mineral constituents stand in such close resemblance.[3] No connection could be established between chemical composition of the waters and the striking differences observed in their radioactive properties.

During the past year the writer has determined the quantity of radium present in several tufa deposits from Hot Springs. The results obtained demonstrate that the quantities of radium present in some of the samples examined greatly exceed the quantity found in the particular sample tested by Dr. Boltwood. Such marked variations as he found in the quantities of radium emanation present in the water samples are likewise exhibited by the tufa samples examined.

The specimens of tufa used for the tests were obtained through the courtesy of Mr. Martin A. Eisele,[4] superintendent of the reservation. He collected them during the past winter, and expressed them to Columbia, Mo., where the writer conducted the tests herewith described in the chemical laboratory of the university.

In determining the radium content of the deposits, the method devised by the Hon. R. J. Strutt[5] in his investigations on the "Distribution of Radium in the Crust of the Earth," was followed in the main. In this process, the material to be tested must be converted into soluble form. As the tufa is calcareous in nature, digestion with hydrochloric acid dissolves most of the material.

[3] Elaborate chemical analyses of the waters of these springs have been made by Mr. J. K. Haywood, of the U. S. Dept. of Agriculture. The published results constitute the greater portion of Senate Document No. 282. See first foot-note.

[4] Mr. Eisele resigned the superintendency, April 1, 1907.

[5] Proc. Roy. Soc., **77**, 472 (1906).

The principal steps of the operation are as follows: An air-dry sample of about 200 grams was pulverized and passed through an 80-mesh sieve. It was then dried for an hour at 105° C. A suitable quantity was then weighed out and dissolved in hydrochloric acid. When the insoluble residue exceeded 2 per cent., it was filtered off, and rejected. Fusion of one of these residues with mixed carbonates of sodium and potassium and subsequent solution and treatment showed that it was practically free from radium. The solution of chlorides was then stored for several weeks in a tightly-corked flask of suitable capacity to permit the accumulation of the radium emanation produced by the radium salts in the solution. After a lapse of a month, when the accumulated emanation had reached a maximum, it was separated from the solution by boiling, the expelled gases being collected in a suitable reservoir.[6] The gas was then transferred to a partially exhausted air-tight electroscope supplied with a reading microscope. From the rate of fall of the charged leaf, the quantity of radium required to produce the emanation in the electroscope, *i. e.*, the radium in the sample, was finally calculated.

The testing apparatus had previously been carefully standardized, by means of a known quantity of radium emanation obtained from a sample of uraninite whose uranium content was known. This method of standardizing electroscopes was first proposed by Boltwood. It is based upon the well-established fact that the radium present in a natural mineral stands in constant ratio to the uranium it contains. The operation of standardizing was carried out as follows: A few mgs. of a standard sample of uraninite were carefully weighed out, dissolved in dilute nitric acid in an apparatus that permitted the quantitative collection of the emanation. The emanation, mixed with other gases, was then introduced into the electroscope to be standardized, and the maximum rate of fall of the charged leaf determined. From these data a factor was computed for the instrument, expressing the quantity of uranium required to produce a fall of the charged leaf corresponding to one scale division per minute of the reading microscope. The uranium values for the activities were then converted into radium values by multiplying by the ratio of

[6] For a description of the apparatus employed and the experimental details, the reader is referred to a former paper by Schlundt and Moore, Jour Phys. Chem., 9, 320 (1905).

radium to uranium. The recent value of this ratio, as again determined by Rutherford and Boltwood, viz., 3.8×10^{-7}, was employed in the calculations.[7]

The same sample of hydrochloric acid served for all the determinations. A blank test showed no indication of radium.

The quantitative results of the radium content of the tufa samples tested are given in the following table: The first column gives the laboratory number, the second the weight of the sample taken for the determination, the third the percentage of insoluble residue, a "small" residue meaning less than 2 per cent. The last column gives the radium found per gram of tufa, the radium unit being 1×10^{-12} gram.

TABLE OF RESULTS.

Laboratory Number.	Weight of sample taken.	Percentage of insoluble residue.	$g \times 10^{-12}$ radium per gram of tufa
1	152 g.	trace	0.72
2A	175	small	26.7
*2B	125	"	26.6
3	100	"	2.62
4A	120	6.7	2.32
4B	98	6.9	2.85
5A	2	9.4	1900.
5B	1	9.4	1927.
5C	2	——	227.
*5D	?	——	1322.
6	160	small	0.73
7	120	8.1	156.0
8	100	5.5	0.56
9	50	18.0	1.18
10	140	small	36.3
11	100	7.8	0.01?
†12	100	——	<0.38

* I am indebted to Prof. Moore, of Butler College, for this determination.
† Sample of tufa examined by Dr. Boltwood. The value given in the table was computed from the quoted statement introduced on page 2 of this paper.

DISCUSSION OF RESULTS.

The most interesting feature of the results obtained is represented in the marked variations in radium content exhibited by the different tufa samples. No chemical analyses of the tufas examined were undertaken, but inasmuch as the physical properties of the specimens varied considerably, differences in composition doubtless exist, notwithstanding the fact that the

[7] Am. Jour. Sci., 22, 1 (1906).

dissolved mineral constituents carried by the water from different springs bear a close resemblance to one another. A few of the samples had a compact crystalline structure and resembled white marble; others were porous, consisting of a framework of travertine intermingled with earthy material, in which some of the higher oxides of manganese are probably present, as considerable chlorine was set free during the digestion with hydrochloric acid. No one physical characteristic or group of physical properties could be singled out, however, as representative of the more active samples. The specimens that left only small quantities of brown oxides when treated with cold hydrochloric acid of four-normal strength were found low in radium; but the presence of a relatively large quantity of insoluble material before the temperature of digestion was raised was found not to be a general accompaniment of high activity. Finally, a careful comparison of the mineral constituents of the spring waters that deposited the tufa of high radium content with those of low values fails to furnish any clue to the marked differences found in their radium content.

As stated before, marked variations in activity also characterize the water samples. Whether a parallelism exists between the content of radium emanation in the waters and the quantity in the tufa deposits cannot be stated, as Dr. Boltwood has designated his samples by laboratory numbers. The same system was followed in this paper upon suggestion of the superintendent of the reservation.

It is seen that the quantities of radium in samples 1, 6, 8 and 9 are of the same order of magnitude as the radium content of the sample of tufa that came to Dr. Boltwood for examination, its maximum radium value being the last figure in the table of results.

Samples 2A and 2B are determinations on the same composite, as are also samples 5A and 5B. In testing specimen No. 5, the calcareous crystalline material was partially separated and tested—5C; its activity was found to be only one-ninth the value obtained for the composite of the entire sample. It therefore appears probable that the radium occurs in pockets, and that it may be associated with some one of the different constituents of the tufa. Further investigations with a view of separating the radium-

bearing constituents, either mechanically or by chemical means, would be of interest.

Another question for further investigation is suggested by the results: Is the radium, found in these tufa deposits, in radioactive equilibrium with its parent, uranium? The quantities of uranium considered here are, in most of the samples, too small to be detected by chemical analysis; but, in sample No. 5 the quantity of uranium would be sufficient for an analytical attempt. With $1{,}900 \times 10^{-12}$ gram of radium there should be associated $1{,}900 \times 10^{-12}/3.8 \times 10^{-7}$ gram uranium, or 0.005 g., *i. e.*, ½ per cent. uranium. Unfortunately, in the course of the preliminary tests conducted with this interesting sample, most of it was lost, and up to the present time arrangements for securing more of the deposit have not been made.

Sample No. 11 does not properly belong in the table. This was a sample of loadstone probably deposited by hydrothermal action at Magnet Cove, Ark., an extinct locality of hot springs in this region.

The number of samples reported here represents but a small fraction, probably less than one-fifth of the deposits of tufa, but the results obtained are of sufficient interest to warrant a more complete investigation. An examination of the underlying sandstones and shales, and the dikes and igneous rock of the locality, would also be of interest in furnishing data as to the source of the radium in the spring deposits.

University of Missouri,
August, 1907.

DISCUSSION.

Prof. Schlundt *(Communicated)*: Dr. Boltwood has kindly communicated the official numbers of the springs that correspond to the laboratory numbers in his paper (l. c.). This courtesy enables me to correlate the activities of the water and tufa samples. The data are summarized in the following table. The values for the activity of the water samples are expressed in grams of uranium per liter of water, as in Dr. Boltwood's paper.

The official numbers of tufa samples *1* and *2* are in doubt, and are therefore not included in the table. Samples number *8* and *9* were tufas taken from caves for which corresponding water samples were not tested.

Laboratory number of tufa sample.	Activity of tufa; $g \times 10^{-12}$ radium per gram of tufa.	Activity of water; $g \times 10^{-4}$ uranium per liter of water.
3	2.62	5.3
4	2.65	12.9
5	1900	3.4
6	0.73	3.7
7	150	26.1
10	36.3	22.0
12	0.38	41.6

The limited number of results thus correlated—there are 50 springs—indicate that a correspondence between content or radium emanation in the waters and radium present in the tufa deposited by the waters does not exist.

A paper read by Prof. S. A. Tucker at the Twelfth General Meeting of the American Electrochemical Society, in New York City, October 19, 1907; President C. F. Burgess in the chair.

THE ELECTROLYTIC SEPARATION OF SILVER AND COPPER.

By H. W. Gillett.

Root[1] gives the following decomposition voltages in ammoniacal tartrate solution at 60°: Ag, 1 volt; Cu, 1.65 volt; H, 1.9 volt. There is evidently some unknown variable, because I obtained the lower values of about 0.65 volt for silver, and about 1.35 volt for copper. At 20°, the values were 0.95 volt for silver, and 1.8 volt for copper. These results made it seem probable that a fairly rapid constant-voltage separation of silver from copper might be effected in ammoniacal tartrate solution.

It was found, by preliminary experiments, that a good deposit of silver was not obtained from an ammoniacal tartrate solution, even with a current density as low as 0.15 amp/dm^2, unless one of the electrodes was rotated rapidly. If either cathode or anode was rotated rapidly enough, a current density of 0.45 amp/dm^2 could be used at 70°. In order to keep the current density low, the runs were made with a Classen dish as cathode and a rotating Classen disc as anode. The silver was determined by weighing, and also by titration of the dissolved deposit, using ammonium sulphocyanate, with ferric alum as an indicator.

The following three runs were made at 70°, the silver and copper being added in the form of nitrates. The solutions, .1032 g. Ag, .1161 g. Cu, 7 g. tartaric acid, and 25 c.c. ammonia (sp. g., .9) per 120 c.c. The voltages were 1, 1.35, and 1.2, and the amounts of silver found were .1033 g., .1026 g. and .1024 g. Runs were next made at 20°, the solutions containing 7 g. tartaric acid and 25 c.c. ammonia per 120 c.c.

[1] Jour. Phys. Chem., 7, 428 (1903).

TABLE I.

Voltage.	Grams Cu.	Grams Ag.	Grams Ag found.
1.35–1.55	0.1161	0.1421	0.1417[1]
1.35–1.55	0.1161	0.1421	0.1424
1.35–1.60	0.0290	0.1421	0.1429
1.35–1.60	0.1161	0.0355	0.0347
1.35–1.53	0.1161	0.0355	0.0344
1.35–1.53	0.1161	0.0355	0.0354
1.35–1.53	0.1161	0.0355	0.0352

[1] Non-adherent, owing to the anode not having been rotated sufficiently rapidly.

A very rapid rotation of the anode is necessary, especially at the lower temperature. If this precaution is not observed, the deposit will not adhere satisfactorily, and too little silver will be found.

It seemed desirable, also, to determine the copper left in the solution. It was hoped that this could be done by raising the voltage, but the copper deposit was bad at all current densities. After a number of experiments, I fell back on the standard method—acidify with HCl, heat nearly to boiling, precipitate the copper by H_2S, filter off the copper sulphide, dissolve in nitric acid containing a little sulphuric acid, filter from the sulphur, and electrolyze with a rapidly-rotating anode and a current density of 2-4 amp/dm^2.

This work was suggested by Prof. Bancroft, and was carried out under his supervision.

Cornell University.

A paper read by Mr. L. H. Duschak at the Twelfth General Meeting of the American Electrochemical Society, in New York City, October 19, 1907; President C. F. Burgess in the chair.

STUDIES ON THE SILVER COULOMETER.

By L. H. Duschak and G. A. Hulett.

I. Introduction.

Chemical decomposition was used at least a century ago as a measure of the electric current, but it was not until Faraday enunciated his laws of electrolysis, in 1833, that the conception of the electrochemical equivalent assumed a definite form, and any real attempt was made to utilize the phenomenon of electrolytic decomposition for purposes of electrical measurement. Of the many systems tried for the purpose, the one involving the deposition of silver from a water solution of silver nitrate was found to possess advantages over all others, and to Poggendorff is due the credit for designing the silver coulometer (or voltameter, as it was then called), which for a considerable time bore his name, and is still used in a form very similar to the original design.[1] It is not within the scope of the present paper to give a detailed history of the silver coulometer; this has been very admirably done in the more recent articles, and it will be sufficient to outline only enough of the development of the subject to connect with it the present work.

Lord Rayleigh and Mrs. Sidgwick,[2] almost simultaneously with F. and W. Kohlrausch,[3] made the first absolute determinations of the electrochemical equivalent of silver which merit attention, and it is through their excellent researches that the silver coulometer became established as an exact scientific instrument. Since this pioneer work, its use has become universal, when an accurate measurement of the electric current is desired,

[1] The coulometer as designed by Poggendorff consisted of a platinum bowl for cathode and a silver rod for anode. The instrument sometimes referred to as the "Poggendorff voltameter," being in reality a modified one due to F. and W. Kohlrausch, has a glass cup placed below the anode to catch the slime. It is of interest to note that in the original design it was recommended that for this purpose the anode be surrounded, either by filter paper or a *porous cup,* both of which schemes have been extensively used, the latter being the approved one to-day. See "Die Lehre von Galvanismus," J. Wiedemann, 2nd ed., 1872, Vol. I, p. 479.

[2] Lord Rayleigh and Mrs. Sidgwick, Phil. Trans., **175** (1884), p. 411.

[3] F. and W. Kohlrausch, Wied. Ann., **27** (1886), p. 1.

and the international ampere is to-day defined in terms of the deposit from the original form of instrument. The silver coulometer has been made the subject of many elaborate investigations, arising from the observation of certain irregularities in its operation and the demand for greater accuracy, but still remains the most reliable instrument yet devised for the measurement of quantity of electricity.

In their original work, Rayleigh and Sidgwick observed that the mass of silver deposited by a given current varied slightly with the conditions of the experiment. Later work, by several different investigators, verified their results, and showed that in general the mass of metal deposited in any type of silver coulometer which permitted the solution from the anode to come in contact with the cathode depended, to a slight extent, upon the particular form of the instrument, the anodic and cathodic current densities, the temperature, and the composition of the electrolyte. These anomalies were partly explained by the excellent work of Richards and his co-laborers.[4-5]

A critical examination of previous investigations convinced them that irregularities were due largely to a subsidiary reaction at the anode, resulting in the formation of some compound, in addition to pure silver nitrate.[6] This view was amply supported by their extensive and painstaking experimental work, and it was shown that the disturbing influence of this peculiar anode product might very simply be avoided by enclosing the anode in a cup of porous porcelain, thus insuring the continued purity of the cathode solution throughout an experiment. The general conclusions which they set forth are entirely confirmed by the later researches of Guthe[7-8] and van Dijk,[9] and without question the silver coulometer after their design, either in the original form or as modified by Guthe, gives more concordant results than any previously-used type of instrument. From a purely practical

[4] T. W. Richards, E. Collins and G. W. Heimrod, Proc. Am. Acad., **35** (1899-1900), p. 123.

[5] T. W. Richards and G. W. Heimrod, Proc. Am. Acad., **37** (1902), p. 415.

[6] A suggestion to this effect had already been made by Novák, Proc. Roy. Bohemian Acad. Sci., Prague, **1** (1892), p. 387; and by Rodger and Watson, Phil. Trans., **186** (1895), p. 631. The former article owing to its publication in the Bohemian language remained apparently unnoticed until noted by Guthe.

[7] K. E. Guthe, Phys. Rev., **19** (1904), p. 138.

[8] K. E. Guthe, Bull. No. 3, Bureau of Standards (1905), p. 349.

[9] G. van Dijk, Ann. Phys., **19** (1906), p. 249.

point of view, great progress has been made, but scientifically, many problems connected with the silver coulometer remain unsettled.

Among the many variables which affect the mass of silver deposited by a given current in the old form of instrument, the gas content of the solution was found to play a decided rôle. Schuster and Crossley[10] showed that deposits made from an air-free solution in vacuo are about one part in 1,000 heavier than those obtained from one saturated with air under ordinary pressure, other conditions being the same in both cases. These authors further observed that an oxygen-saturated solution gave a deposit distinctly lighter than that obtained in air. Experiments along the same line by Meyers[11] show precisely the same difference between deposits in air and in vacuo, and further establish the interesting fact that in an atmosphere of nitrogen the deposit exceeds that in air by about 6 parts in 10,000. (He also showed that a solution saturated with carbon dioxide gives a deposit lighter by approximately 5.5 parts in 10,000 than that in air.) Merrill[12] tried the effect of an air pressure of about 100 atmospheres on the silver coulometer, but the few published results permit no definite conclusion. Finally, Richards and Heimrod[5] (p. 430) state, without giving the experimental data, that their investigations along the same line verify the above-mentioned results. This may all be summed up by saying that in general the less oxygen the solution contains, the heavier will be the deposit from it; for, from the chemical nature of the element, nitrogen, in all probability, may be regarded as simply diluting or excluding the first-mentioned gas.

Several ideas have been advanced to explain this peculiar phenomenon. Schuster and Crossley[10] (p. 357) suggest that the dissolved gases might assist in conducting the current. In order to fit this explanation to the facts, it is necessary to assume that oxygen plays a much greater rôle than nitrogen. This is not hard to believe, but there is no clear-cut evidence to show that such is the case in the silver coulometer. Another idea advanced by the same authors, that in the presence of oxygen silver might

[10] A. Schuster and A. W. Crossley, Proc. Roy. Soc., **50** (1892), p. 344.

[11] J. E. Meyers, Wied. Ann., **55** (1895), p. 288.

[12] J. F. Merrill, Phys. Rev., **10** (1900), p. 167.

be dissolved by the electrolyte, seems more probable, but again lacks experimental confirmation.

In casting about for an explanation, it must be borne in mind that both Schuster and Crossley, who worked with the filter-paper coulometer, and Meyers, who used the Kohlrausch pattern, in which a glass dish is suspended beneath the anode, employed forms of instruments which permitted the free diffusion of the anode liquid. That is, this effect due to dissolved gases has been observed only under conditions such that the cathode solution contained the products of the irregular anode reaction and would normally yield a deposit heavier than that from pure electrolyte. A moment's consideration of this fact suggests that an explanation of the whole phenomenon may be found in some action of the dissolved oxygen upon the anode product resulting in its total or partial destruction. This is the view taken by Richards and Heimrod, and one which seems entirely reasonable.

If this can clearly be shown to be the case, a careful study of the action of these gases may perhaps lead to a more exact knowledge of the peculiar reaction at the anode and of the product there formed. Before this can be undertaken, however, an important question must be answered, namely, does the mass of silver deposited from a perfectly pure solution of silver nitrate depend at all upon the presence of these gases (N_2, O_2, CO_2) in the electrolyte? In other words, will the porous-cup coulometer show any variation in vacuo or in atmospheres of the several gases? It was with a view primarily to obtain some information on this point that the present investigation was undertaken. This paper covers only the work on deposits in vacuo and nitrogen, but in the course of it another question connected with the silver coulometer has been examined at some length.

II. General Method and Apparatus.

The method of experiment was in general comparative. Two similar instruments were operated in series, one under the conditions to be investigated, and the second, which was always taken as a standard, in air. Some preliminary experiments, in which accuracy of about 1 part in 10,000 was obtained, and which

it is not worth while to describe in detail, suggested that the porous-cup coulometer yielded a deposit in vacuo and in an atmosphere of nitrogen slightly lighter than that in air, but the results were too irregular to permit any definite conclusion. More than anything else, the preliminary work served to indicate that before any significance could be attached to the slight difference observed between two deposits under different conditions, the limit of experimental error must be accurately known, and further, that this limit of error must be less than 1 part in 10,000. A survey of the literature confirmed this view in furnishing many examples of cases where the interpretation of results was doubtful because of the large and uncertain experimental error.

The best balances and many methods of electrical measurement, particularly of resistance and electromotive force, are sensitive to 1 part in 100,000, or better, and if the silver coulometer is to be classed as a precision instrument, and especially if it is to be taken as a material standard in electrical work, it should possess an accuracy equal to these. A reproducitility of 1 part in 10,000 has been claimed for the porous-cup coulometer and adequately demonstrated in the best previous researches. But, as just pointed out, this is not all that could be desired, and, with a hope of attaining a greater accuracy, a careful study of the experimental method was made. The few duplicate experiments so far performed indicate that this has been accomplished, and so it seems worth while, before taking up the experimental work bearing directly on the question under investigation, to give a detailed account of the apparatus and method eventually employed.

The form of porous-cup coulometer used was very similar to the original design of Richards and his co-workers. The two instruments, to be designated as I and II, are shown arranged as for an experiment in Fig. 1, and in Fig. 2 one has been dismantled to exhibit the different parts. The cathodes were two cylindrical cups of platinum, 10 cm. high and 5 cm. in diameter, weighing I, 73.2 g., and II, 74.7 g. Filled to within 1 cm. of the top, the capacity of each was 177 c.c., and the cathode area, 161 sq. cm. The inner surfaces had been etched with aqua regia, sufficiently to remove the bright burnish, and also slightly scratched by rubbing with sea sand.

The porous cups were made by cutting the tops off Pasteur filter tubes. They were 11 cm. long, 2.4 cm. in diameter, and were supported by triangles of glass rod, with projecting corners, which were attached about 1 cm. below the top by platinum wires passing through small perforations in the walls. The projecting corners of these triangles rested in notches cut in the top of the cylindrical glass jackets which surrounded the cathodes.

These jackets were cut from tubing having an internal diameter about 3 mm. greater than the platinum vessels, so that an annular space of a little over 1 mm. remained between the platinum and the glass. They were 11.8 cm. high, and, in addition to holding the porous cups securely in place, protected

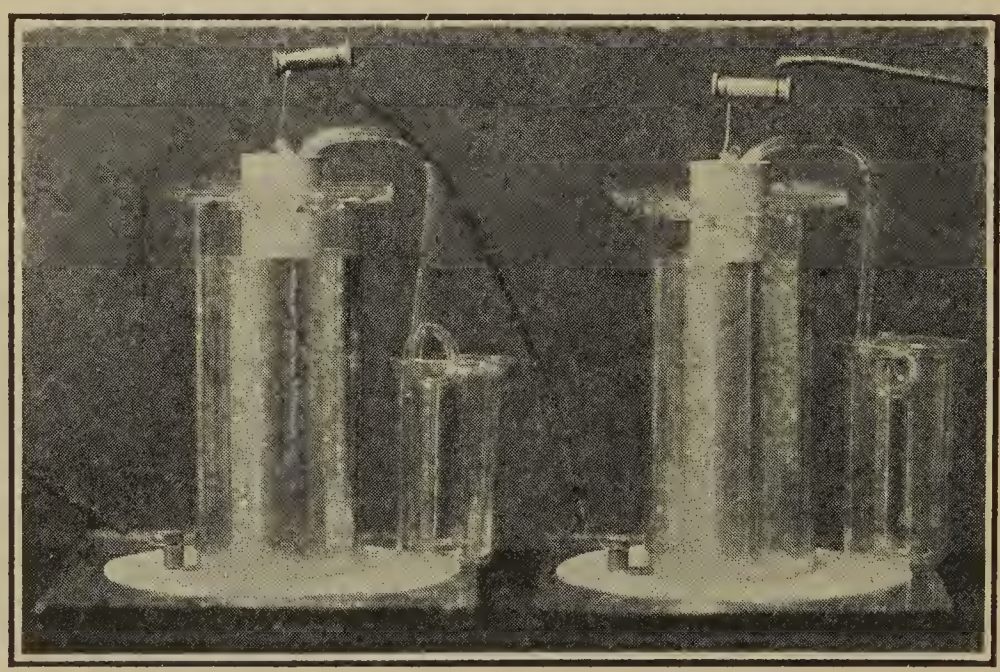


Fig. 1.

the cathodes from all dust and dirt. Rectangular pieces of glass plate, cut out to fit around the porous cups, served as covers for the instruments, and kept the cathode solution free from all contamination.

Pure electrolytic silver, cast in rods 6 cm. long and 1 cm. in diameter, served as anodes. They were suspended, and electrical contact was made by rather stiff pieces of platinum wire which hung from short, slightly bent pieces of glass rod resting on the edges of the porous cups.

For the purpose of removing the anode solution from the porous cups and maintaining it at a level lower than the solution without, a so-called "constant level" siphon was devised. This

was an ordinary siphon, with the addition of a small loop near the delivery end, the upper bend of which was perforated by an opening slightly larger than the cross-section of the tube. When in operation, liquid filled the siphon around to this orifice, and if the level in the containing vessel rose ever so slightly above this point, a flow of liquid at once resulted. These siphons were obviously entirely automatic in operation, and their use avoided the inconvenience, mentioned by other workers, of frequently removing portions of the anode solution. The inner end of each siphon, which was notched for the easy ingress of liquid, rested

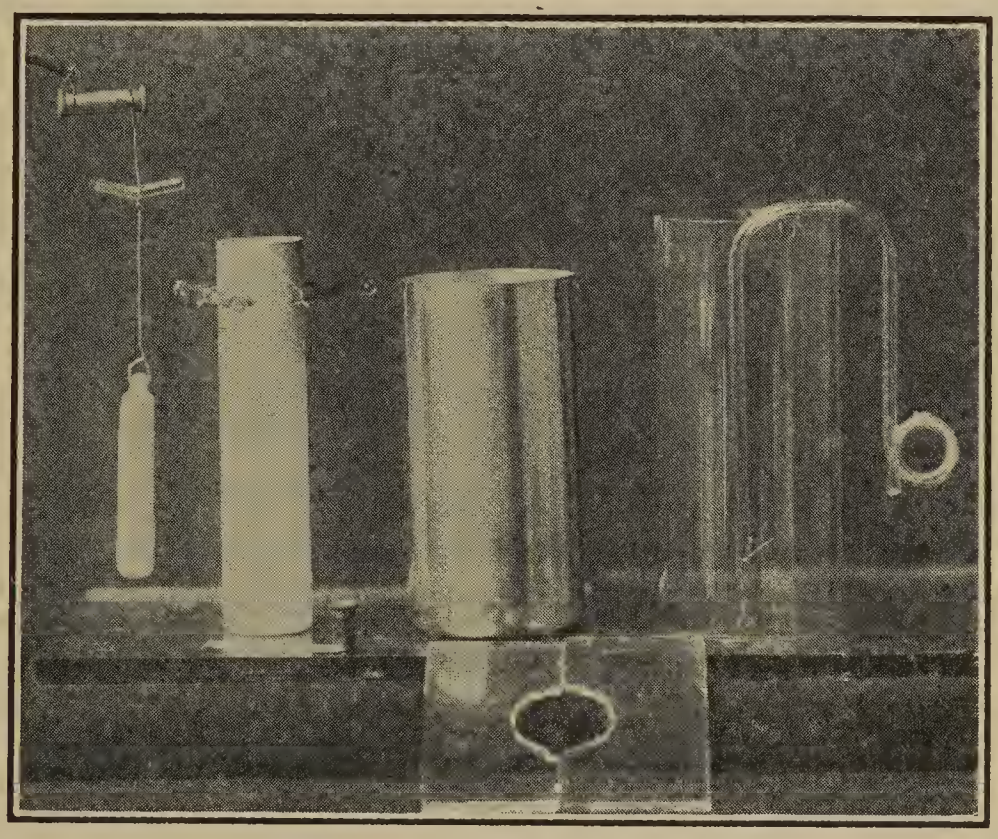


FIG. 2.

on the bottom of the porous cup, thus removing the heaviest of the anode solution. The dimensions were such that the surface of this solution was maintained 1 cm. below that next the cathode, and it is believed that this difference in level was sufficient to prevent outward diffusion. Small beakers served to collect the anode liquid which continually dripped from the siphons during an experiment. Electrical contact was made with each cathode by means of a strip of platinum foil placed beneath and bearing a binding screw on its outer end.

This form of instrument is entirely self-contained, requiring

no external support for any of its parts, and the glass jacket, etc., form ample protection against dust and dirt, and supply the necessary insulation where needed.

For all except the experiments in vacuo, both instruments were mounted, as seen in Fig. 1, on separate squares of thick glass plate, which, in turn, rested on a rubber mat. Two or three sheets of filter paper were placed beneath the instruments to quickly absorb any drops of liquid which might accidentally fall. In the majority of experiments, a third coulometer of the porous-cup type, as designed by Guthe[7] (p. 140) was operated in series with these two, but as it served only for miscellaneous preliminary experiments, it does not seem worth while to describe it in detail. The current was furnished by a battery of five storage cells, arranged in series with an ammeter, key and regulating resistance. The entire circuit was well insulated, and every precaution was taken to prevent leakage about the coulometers, the connections between them and the leads directly to and from them being air lines.

III. Experimental Manipulation.

Attention is next directed to the question of manipulation. The treatment of the two (or sometimes three) instruments was in all cases identical, and the method here outlined is the one used in the final series of fourteen experiments. The preparation of apparatus and materials for an experiment will be taken up first.

In regard to the cathodes, the previous silver deposit was either removed with dilute nitric acid, or scraped out with a small platinum spatula. In either event, the platinum vessels were submerged for at least one hour in a bath of hot (95°-100°) concentrated nitric acid. They were then washed thoroughly with distilled water and placed to drain upon supports of nickel wire. The major portion of water adhering to the outside of the vessels was removed with filter paper, which was allowed to touch the surface as little as possible, and they were left to dry partially in air. For protection against dust, large beakers were inverted over the cathodes, and supported to permit the easy escape of water vapor. In this, as in all subsequent manipulation, the platinum cylinders were never touched with the fingers, but

handled entirely with clean brass tongs made especially for the purpose. The method of drying was somewhat different from the usual one, and was, of course, the same for the cathodes alone or with deposited silver.

Instead of heating the platinum cups, as usual, in an air bath at 160°, the final drying was done in vacuum desiccators. For this purpose, ordinary vacuum desiccators were employed, a separate one for each coulometer. The platinum vessels stood on nickel wire supports in clean glass beakers, which rested securely in the central wells of the desiccators. The annular space about each beaker was partly filled by coarse, dust-free, anhydrous calcium chloride. After this method had been in use for some time, it was discovered that it had been previously employed by Potier and Pellat[13] and Leduc.[14]

After the platinum vessels had stood in the air about half an hour, or until the outer surfaces were quite dry, they were, if necessary, lightly gone over with a soft camel's hair brush to remove bits of dust and fibers from the filter paper, and placed in the desiccators, which were at once evacuated to about 20 mm. They were allowed to stand in the desiccators, in the balance room, for at least four hours, then air filtered through clean cotton was slowly let in, and they were weighed.

The porous cups were originally cleaned by soaking for some time in hot concentrated nitric acid, and then washed by allowing hot distilled water to percolate through them until every trace of acid was removed. From time to time, in the course of the work, they were cleaned with dilute nitric acid to remove traces of silver stain. Between experiments, the porous cups were kept submerged in beakers of distilled water. The anodes, to start with, were etched by nitric acid until the bright metal was exposed, and from time to time, as they became coated with the dark anode slime, this treatment was repeated.

The electrolyte was invariably made by dissolving 15 parts of silver nitrate in 85 parts of distilled water. The salt used was either Kahlbaum's best, which was assumed to be pure, or some re-crystallized from water and heated to a temperature just below the fusing point to remove all excess of acid. The entire

[13] Potier et Pellat, Jour. de Physique, IX (1890), p. 381.

[14] M. A. Leduc, Jour. de Physique, [IV] 1 (1902), p. 561.

quantity of solution for an experiment was made in one lot the day before it was to be used, and allowed to stand over night in a Jena flask, so that any reaction between the silver nitrate and any possible impurities in the salt or water might come to an end. It was usually tested with sensitive litmus paper. Shortly before use, the solution was filtered through a layer of carefully-purified asbestos in a Gooch crucible and examined in a bright light to insure freedom from any bits of dirt or asbestos fibers which might have passed through the filter. The solution was carefully guarded from dust and from all contact with organic matter of all kind. The distilled water used contained considerable dissolved air, and the agitation incident to the solution of the salt and filtration was considered sufficient to complete the saturation.

The actual execution of an experiment, for example, duplicates in air, was quite simple. The apparatus was arranged as already described, and the transfer of solution accomplished entirely with pipettes. After introducing the cathode solution, the porous cups, freshly rinsed with distilled water, were put in place, partly filled, and the siphons at once set in operation. Finally, the electrical connections were made, and after waiting several minutes to permit the electrolyte to diffuse into the porous cup, the key was closed and the current adjusted to its proper value. In all experiments, a current of about .31 ampere was employed and allowed to flow for four hours, thus depositing about 5 g. of silver. The average cathodic current density was about .002 amperes per sq. cm. That at the anode varied, of course, with the extent of the corrosion of the latter, and is of little importance, since the anode liquid was excluded from the cathode solution. The room temperature varied from 20° to 25°. During the first few minutes of an experiment, the resistance of the instruments always decreased slightly, due probably to the further diffusion of the electrolyte into the porous cups and a possible slight rise in temperature. Towards the end, there was a slight increase, which may be explained by the gradually increasing dilution of the cathode solution as the experiment proceeded. The resistance of each instrument was about 2 ohms. Once or twice, in the course of the four hours, fresh solution was added to the cathodes to replace that which had diffused into the porous cups.

At the termination of an experiment, the porous cups, anodes, etc., were at once removed, and the outer surfaces of the former examined for possible bits of loose silver, which, however, were never found. About four-fifths of the solution from each coulometer was carefully siphoned off into a clean beaker, and the remainder poured into a second. The deposits were then washed with three or four small portions of distilled water, the washings being collected in a third set of beakers, and, finally, the platinum vessels were filled with water, and, having been covered by inverted beakers, were permitted to soak out over night. In the morning, this water was removed and tested with potassium iodide, and if any turbidity was observed (which occurred rarely), the deposits were washed several times more, otherwise only once. The cathodes were then covered as before for partial air drying. Alcohol or other organic liquid was never used for washing. The possible advantage of slight time-saving where speed is not the first essential, seemed more than outweighed by the danger of contaminating the deposits, unless great pains were taken in the purification of the liquid. Neither was it deemed advisable to use hot water, as is sometimes recommended.

The solution and wash water from each instrument were carefully examined in a bright light for loose bits of silver. None were ever found in the first large portion of electrolyte which had been siphoned off, but a few were usually discovered in the second portion of solution and in the wash water. The quantity was quite variable, and in a few cases none at all was found. The silver particles were collected in a Gooch crucible on a small disc of filter paper, which was easily removed by a pointed glass rod and incinerated in a minute crucible at a low heat. Later, they were added to the proper deposit. The platinum cylinders were lightly brushed, placed in desiccators, as before described, and, after at least four hours' drying, weighed.

The appearance of the deposits calls for no particular comment. They were made up of small, compact silver crystals distributed quite uniformly over the greater portion of the cylindrical surface. Toward the top and on the bottom and corners, the crystals were more scattering.

IV. Weighing.

The question of accurate weighing received considerable attention.[15] The balance employed was a short-arm Reuprecht analytical balance, gold plated and made for a maximum load of 200 g. It stood upon a stone ledge in a special balance-room having no outside walls, so that the temperature suffered only gradual changes. An extra glass case was placed about the balance to further assist in preventing the sudden temperature variations which are responsible for most of the trouble in ordinary weighing. A single 32 candle-power incandescent light, symmetrically placed above and in front of the balance about 25 meters distant, furnished the only illumination. This was kept burning continually. The beam of the balance was of "magnalium," each side being divided into 100 parts, so that with the 2 mg. rider used, one division corresponded to .02 mg. A large reading lens within the case was used for observing the swings of the pointer, and with a little practice, tenths of a division on the scale could be readily estimated. With a 100-g. load, the pointer reflected 10 divisions for 1 mg., so readings could be made directly to hundredths. A thermometer and accurately-calibrated hygrometer were hung within the case, and during damp weather a small dish of calcium chloride was sometimes set within to maintain the humidity at about 33 per cent. The variations from this value were rarely more than 6 to 10 per cent. The weights (brass, gold plated) were, of course, very carefully calibrated, and the whole set, totaling 100 g., compared with a 100-g. standard weight. The calibration of the platinum fractions was based on the brass grams, and, within the usual ranges of temperature and pressure variations, it was not necessary to apply a correction for the difference in density. From time to time, in the course of the work, the weights were re-tested, and the comparison with the 100 g. standard repeated, so that any change in them could not remain long undetected. No variation, however, was observed.

All weighings were made by the method of substitution. The platinum vessel to be weighed was placed on the right-hand pan, weights from an old set in slight excess added to the left, and

[15] Many valuable suggestions in regard to accurate weighing were gained from the excellent treatment of the subject by Landolt, Zeit. f. Phys. Chem. **55** (1906), p. 589.

then a few small weights from the calibrated set added to the right for approximate equilibrium. The two balance cases were then closed, and at least half an hour allowed for conditions within to come to equilibrium. Experiment showed that twenty minutes was sufficient for this, but a safe margin was allowed. At the end of this period, the temperature and humidity within the case and the barometric pressure were observed; a final adjustment of the rider was made, and two or three sets of swings from *separate* releases of the beam observed. Calibrated weights were then substituted for the platinum vessel, the cases were closed for five minutes, and swings observed as before. The sensibility was determined from time to time, but remained practically constant. The weighings were all corrected to vacuum, account being taken of variations in atmospheric density. The use of similar platinum vessels for tare would, of course, have avoided this trouble, but they were not at hand, and therefore a table of corrections was calculated extending over the usual range of thermometric and barometric variations and based on the air one-third saturated with water vapor. In making this calculation, the density of the platinum was assumed to be 21.5, and of the brass weights, 8.4. The largest probable deviation from these assumed densities could introduce no significant error. A similar table of corrections was calculated for silver weighed with brass weights. All weighings were repeated, and, except in a very few rare cases, duplicates agreed within .01 or .02 mg.

In the course of the work, several factors disturbing accurate weighing came under observation, and a mention of a few of them would, perhaps, be of interest. Temperature variations, of course, are the most prolific source of trouble, and they arise in many different ways. For example, a change in the illumination of the balance produced a marked effect.

A second 32 candle-power light (in addition to the one kept burning continually) was symmetrically situated about 1 m. from the balance. If this was turned on when one of the platinum vessels was on the balance, an apparent loss of weight at once manifested itself, reaching .2 mg. in the course of two minutes. When either the light was extinguished or the platinum vessel shielded from its radiation, the former equilibrium was

in a short time restored. With equal platinum dishes on the balance pans, the turning on of the light had no effect, but if one was screened, the other, still illuminated, showed, as before, an apparent decrease in weight. The most obvious explanation is that the radiant energy from the light falling on the platinum surface raised its temperature slightly, and thus set up air currents which made it appear lighter.

Trouble due to electrical charges was encountered only once, when the balance pans had been gone over with a camel's hair brush.

No disturbance arising from the varying humidity of the air was observed, and this came into consideration only through its effect upon atmospheric density. On a few occasions, there was a suggestion of some slight systematic variations in the weighings which could not be traced to any definite cause, but was quite probably due to some slow change in temperature.

V. Experimental Error.

The question of the error obtaining in the method of experiment adopted falls into two parts, namely, its magnitude and distribution. Since trials with the two coulometers in series could answer only the first part of this question, further tests were necessary.

It has been suggested that a possible source of error exists in the non-recovery of the loose silver particles usually present in the solution and wash water from the coulometers[14] (p. 265). To determine the size of those which might easily escape the vigilance of the operator, some silver wire, .024 mm. in diameter, was cut into sections from .5 to 2 mm. in length and thrown into water in a beaker similar to those used in collecting the washings. The smallest bits were readily visible and were with ease collected on the filter, as previously described. A section of wire 1 mm. long has a mass of only .0047 mg., hence, it follows that any weighable silver crystals may be easily recovered, and with quite ordinary care no error can arise from this source.

With a view to gaining some information as to the limit of error obtaining in the manipulative process as a whole, several so-called "manipulation tests" were made at different times. The two instruments were submitted to treatment identical in

every way with a regular experiment, with the one exception that no electricity was passed through them. In the tests in which the cathodes carried silver deposits, there were always some loose crystals in the solution and washings which had to be recovered in the way outlined. The results of these tests are given in Table I. The numbers indicate the change in weight entailed by the treatment, + for a gain, and — for a loss.

TABLE I.

Manipulation Tests.

No.	I.	II.	REMARKS.
	Mg.	Mg.	
1	±0.00	+0.03	Without deposit.
2	+0.14	±0.00	With 10 g. silver deposit.
3	—0.02	—0.05	" " " "
4	—0 02	—0.01	" 5 g. " "
5	+0.04	+0 03	Without deposit.

Aside from Test 2, with coulometer I, which is unusually large for some unknown reason, the variations are not much larger than some possible error in the weighing and, in general, in the same direction for both instruments. It is of interest to note that the empty cups showed a gain, and those with deposits a loss. This latter suggests a slight solvent action of the solution and wash water on the deposits, but it is too small to be of much significance. These results serve to indicate that the probable error in the entire process of manipulation, is less than .05 mg.

One further point connected with the experimental method may perhaps be mentioned before the actual experiments are considered. Since the method of drying the cathode differed from the usual one, a comparison between them seemed worth while. At the termination of an experiment, the two platinum vessels, each containing 5 g. of silver, after being dried in vacuo and weighed, were heated two hours in an electric furnace at 150°-160°. Cathode I showed a loss of .11 mg., and II of .07 mg. Another time, the clean cathodes, after having been prepared for an experiment by the method described, were heated three

hours each in the electric furnace at 160°. Cathode I lost .03 mg., and II, .05 mg. These were then used in a regular experiment, in which 5 g. of silver were deposited, and, after vacuum drying and weighing, were again heated for three hours at the same temperature. Cathode I lost .03 mg., and II, .01 mg.

Apparently, so far as results are concerned, there is very little difference between the two methods, and none which need be considered when comparative and not absolute results are required. If, however, as is usually the case, the drying is done in a gas-heated air bath, there is danger of contaminating the deposit with the products of combustion unless special precautions have been taken. One way of avoiding this danger was to use an electric oven, as was done in the present instance. Another and simpler way is to employ the method of vacuum drying, which offers the surest way of avoiding all contamination of the silver from any cause whatsoever. Further, the service of this method throughout the work and the "manipulation tests" have demonstrated its constancy, and so, for simplicity and convenience, as well as for the reasons mentioned above, it is to be preferred to the usual method.

VI. Test of Constancy of the Coulometers.

Turning now to the actual coulometric work, attention is first directed to the duplicate experiments in air. The masses of the deposits obtained from the two instruments under precisely similar treatment are given below.

Table II.

Duplicate Experiments in Air.

No. of Exp.	Deposit in I.	Deposit in II.	Diff.	Diff. Per Cent.	Remarks.
	Grams.	Grams.	Mgs.		
1	5.11864	5.11862	0 02	0.0004	Deposit on platinum.
2	5.05505	5.05515	0.10	0.0020	" " silver.
5	5.00568	5.00569	0.01	0.0002	" " platinum.
6	5.00778	5.00806	0.28	0.0056	" " silver.
7	5.01033	5.01030	0.03	0.0006	" " platinum.
8	5.17554	5.17553	0.01	0.0002	" " "

The agreement between the deposits formed on clean platinum cathodes (Experiments 1, 5, 7, 8) is quite remarkable, being distinctly better than 1 part in 100,000 in every case. The average difference in these four experiments is .0004 per cent., which is less than that observed in any previous work. Richards and Heimrod[5] found an average error of .004 per cent., and the results of other investigators show about the same order of agreement. Perhaps four experiments are rather few from which to draw general conclusions, but it is confidently believed that the agreement shown is more than accidental. If this be true, the porous-cup form of silver coulometer is capable, under proper conditions, of a very high degree of accuracy—an accuracy equal to that attained in the process of weighing alone.

The two experiments in which the deposits were formed on the silver from a previous run do not show such good agreement, and, for this reason, in all subsequent work clean platinum cathodes were invariably used. Apparently, a new source of error arises when a silver-coated cathode is used, but this is mentioned only in passing now, and will be referred to again later on.

It may be mentioned that the results just given include *all* the duplicate experiments in air, obtained with instruments I and II. The third coulometer mentioned before, of the porous-cup type proposed by Guthe[7] (p. 140), furnished, as the average of six experiments in air, a deposit .002 per cent. lighter than that obtained in one of the other instruments (both cathodes being clean platinum), and showed an average difference of .004 from the same. The cathode area was about two-thirds that of the others, and the porous-cup was not quite so fine-grained. The reason for this lack of constancy is not known.

VII. The Effect of Vacuum.

Now that the accuracy of the method had been demonstrated, the original problem mentioned in the introduction (p. 260) was taken up. The experiments in vacuo first claim attention. One instrument was, of course, operated in air, and the other in an evacuated receptacle. For this purpose, the receiver of a large Bruehl apparatus served admirably. One lead-wire passed through the center of a solid rubber stopper placed in the tubular

at the top, and the other entered similarly through a second tubular on the opposite side, near the bottom. The wire within was rubber-coated, and the inner ends of the rubber stoppers and the glass in the vicinity were coated with paraffin. A stop-cock fitted in the tubular in the cover served for the exhaustion and admission of air. The coulometer within rested on a glass plate, which was paraffined on the under side and supported on sections of paraffined cork.

Before each experiment, the receiver was dried out by evacuating with a dish of calcium chloride inside. The porous cup to be used was also evacuated in a beaker of distilled water for some time, to remove, so far as possible, the air bubbles from the walls. The anode siphon was cleaned with chromic acid, so that the solution would wet it completely and avoid the air film which might cause it to fail in vacuo. As mentioned before, the solution for both instruments was made up together, and, after filtration through asbestos, the part for the vacuum work was evacuated in a Bunsen filtering flask. The 18 or 20 mm. used usually caused the solution to boil at first. It was kept under low pressure for several hours, with a very slow stream of air bubbling through to keep it stirred, and from time to time it was well shaken.

When all preparation had been made for an experiment, air was quickly let into the flask, and the necessary quantity of solution transferred to the coulometer with a pipette. Care was taken to disturb the surface as little as possible, and all unnecessary contact with air was avoided. The coulometer in vacuo was arranged precisely the same as the one in air, with the addition of a small crystallizing dish with minute connecting siphon arranged to supply solution to the cathode to replace that diffusing into the porous cup. A small beaker containing anhydrous calcium chloride was always placed beside the instrument, to prevent the rarefied atmosphere from becoming saturated with water vapor, and thus avoiding the possible danger of any current leakage about the walls due to the condensation of a moisture film upon them.

After all had been arranged, the cover of the receiver was put in place, made tight with a film of stop-cock lubricant, and the evacuation carried to within a few millimeters of the vapor

pressure of the solution. This, of course, varied with the temperature, and, in general, the pressure ranged from 20 to 25 mm. As before, a current of about .31 ampere was used. In the course of the four hours consumed by the experiment, it was usually necessary to decrease the vacuum for periods of several minutes three or four times, in order to allow bubbles forming in the anode siphon to pass out and not interrupt its operation. Occasionally, the receiver had to be opened for a short time, but this could not measurably affect the experiment, since the absorption of gas by a quiet liquid is very slow. At the end of the four hours, the current was broken, and the experiment completed as before. No evidence of gas generation at the anode was ever observed. In regard to distribution and texture, the deposits in air and in vacuo were quite similar. The results of the vacuum experiments follow:

TABLE III.

Porous Cup Coulometer in Air and in Vacuo.

No. of Exp.	Deposit in Air.	Deposit in Vacuo.	Diff.	Diff. Per Cent.	REMARKS.
	Grams.	Grams.	Mg.		
3	5.02576	5.02558	+0.18	0.0036	Deposit on platinum.
4	5.04893	5.04866	+0.27	0.0054	" " silver.
9	4.99939	4.99895	+0.44	0.0088	" " platinum.
10	5.02800	5.02810	—0.10	0.0020	" " "
11	5.03180	5.03134	+0.46	0.0092	" " "
12	5.04563	5.04516	+0.47	0.0094	" " "

The several experiments do not show the agreement which might be desired. In Experiment 4 the cathode carried a previous silver deposit, which decreases the significance of the result. *A priori* there was no reason to discard Experiment 10, but a subsequent examination showed that both the air and vacuum deposits were stained black in many places, and so the result is open to question. The cause of the black spots is not known, and the result is given for the sake of completeness. The exact magnitude of the difference between deposits in air and in vacuo is perhaps still left in doubt, but the existence of such

a difference can scarcely be questioned. Evidence corroborating this, adduced from an examination into the purity of the silver deposits will be given later. In all these experiments, the temperature, cathodic current density, and concentration of solution were the same, and it seems possible that a change in these conditions might vary the result. This is one of the questions which should be tested by further experiment.

It appears, then, that the deposit in the porous cup coulometer in vacuo and from an air-free electrolyte is distinctly lighter than that in air. This was something of a surprise, since experiments with the old form of coulometer show precisely the opposite, namely, a heavier deposit in vacuo. But, it must be remembered that in the latter case the electrolyte is *not* pure silver nitrate solution throughout an experiment, and the activity of the anode product could easily mask this new "vacuum effect," which is not greater than 1 part in 10,000.

The problem of explaining this phenomenon at once presents itself. It could be accounted for very simply by a slight leakage of current within the apparatus, and this question, first of all, demands a definite answer. The insulation within appeared to be exceedingly good, but the resistance across a glass surface varies widely with the humidity of the air in contact, and since the rare atmosphere within the apparatus was probably nearly saturated with water vapor, it seemed quite possible that the explanation just suggested was the right one. The leakage of .01 per cent. of the current used, that is, of .00003 ampere, would entirely explain things. The fall of potential through the vacuum apparatus was about .7 volt. Hence, to produce this leak, the insulation resistance would have to be, roughly, 25,000 ohms. Tronton and Searle[16] have studied the leakage across glass surfaces in atmospheres having a humidity up to 80 per cent., and an examination of their results for a nearly saturated atmosphere shows that at least the resistance must have been several megohms.

It seemed best, however, to make a direct test. This was done by arranging the coulometer with solution, and all exactly as for a regular experiment in vacuo, except that a sheath cut from the bottom of a large test tube and paraffined on the outside was

[16] F. T. Tronton and C. Searle, Phil. Mag., **12** (1906), p. 336.

slipped over the porous cup. This sheath extended about 1 cm. above the surface of the cathode solution and formed the only break in the usual circuit through the apparatus. The pressure within was then reduced to 25 mm. (room temperature was 25°), and from time to time, in the course of five hours, the resistance between the two leads was tested with a delicate Wheatstone bridge arrangement. Every trial showed that the resistance was greater than 15 megohms, which was the upper range of the apparatus. The electromotive force applied was 1.5 volts, and when a known resistance of 2 megohms was put in shunt with the vacuum apparatus, a change of a few thousand ohms produced a marked deflection of the galvanometer. Because of the rather high room temperature, the inner surface of the receiver soon became coated with a visible moisture film; hence, the test was quite severe, and showed conclusively that there could have been no measurable leak.

There is, then, a real difference between the deposits, and the problem of explaining this peculiar "vacuum effect" once more presents itself. The suggestion due to Merrill,[12] that the change in pressure might alter the capacity of the ions, lacks both theoretical and experimental support, and is scarcely to be considered, unless more probable attempts at explanation fail. It is conceivable, though, that if the deposit is not absolutely pure silver, the amount of impurity, for example, included electrolyte, might depend on the pressure, owing to its effect on the texture of the deposit. Any such explanation, however, is rather far-fetched, and certainly the most probable one is to be sought for in some effect connected with the air content of the solution.

This factor might, of course, operate in several different ways. If the dissolved gases assisted in conducting the current, as has been suggested[10] (p. 259), a lighter deposit would have been found in air, and not in vacuo, as was actually the case; so, apparently, the air plays some other rôle.

Bose[17] has advanced the idea that the atmospheric oxygen occluded by a platinum surface might be depolarized when the surface is made the cathode in the silver coulometer, resulting in a too small deposit of silver. This, similar to the last con-

[17] E. Bose, Chem. Ztg., 26 (1902), p. 67.

clusion, would appear to explain precisely the reverse of the phenomenon observed, and therefore does not apply to the case in hand.

It seems improbable that so inert a substance as nitrogen could have any other effect than to simply dilute the oxygen, and one is inclined to believe that this more active element is responsible for the facts observed. The further pursuit of this line of inquiry leads quite naturally to another part of the general problem mentioned in the introductory paragraphs, namely, how will the deposit from a nitrogen-saturated solution compare with that from one containing air? This question was submitted to experiment.

VIII. The Coulometer in Air and Nitrogen.

For the work in nitrogen, the two instruments were arranged as for duplicate experiments in air. It was not thought necessary to place the one for the nitrogen-saturated solution in a closed receiver, but instead, a small capillary tube was attached, opening below the porous cup, so that a slow stream of nitrogen could be bubbled through the electrolyte during an experiment. The solution was freed from air exactly as for the vacuum experiments, then saturated with nitrogen, and alternately evacuated and saturated a few times. Finally, it was thoroughly saturated and left under a slight pressure of gas for some time. Table IV gives the results obtained.

Table IV.

Porous Cup Coulometer in Air and Nitrogen.

No. of Exp.	Deposit in Air.	Deposit in N_2.	Diff.	Remarks.
	Grams.	Grams.	Mgs.	
13	4.97938	4.97832	+1.06	Deposit on platinum.
14	4.99152	4.99103	+0.49	" " "

The nitrogen for Experiment 13 was prepared by passing a mixture of air and ammonia over a bright copper spiral at a red heat, and then through several wash bottles containing sulphuric acid, to remove the excess of ammonia. A considerable quantity of the gas was bubbled through a test tube of Nessler's reagent

without giving any indication of the presence of ammonia. However, just before the solution saturated with the gas was used for the experiment, a faint suggestion of turbidity was noticed, and a test with litmus paper showed it to be faintly alkaline. Subsequently, a large volume of gas was washed with a small portion of water by repeated evacuation and saturation, and in this water a minute trace of ammonia detected. Since all preparation had been made for the experiment, it was decided to carry it through with the impure gas. A few drops of dilute nitric acid were added to the solution, making it as nearly neutral as possible, and the experiment continued. A test of the used solution, the following morning, showed it to be very faintly alkaline, and a film of dark-brown precipitate, probably silver oxide, had collected on the bottom of the containing beaker during the night. The appearance of the deposit differed slightly from the usual one, the silver crystals being finer and grown out more from the cathode. The presence of silver oxide in the solution, together with the more spongy appearance of the deposit, would lead one to expect an excess of weight. The contrary was the case, but the experiment does not deserve much consideration.

The nitrogen for Experiment 14 was formed by the decomposition of a faintly acid solution of ammonium nitrite containing a little potassium bichromate. The gas was passed over a long spiral of bright copper gauze heated to redness, and is believed to have been perfectly pure. The deposits in air and nitrogen had a perfectly similar appearance, and the experiment seemed trustworthy in every way. It is of interest to note that the difference between them is the same as that obtained in several experiments in vacuo. It would, of course, have been desirable to perform several more experiments with nitrogen, and particularly to investigate the effect of saturating the electrolyte with oxygen. Unfortunately, it was necessary to interrupt the work at this point, but it is hoped that the whole question may be more extensively studied in the future.

The evidence so far accumulated seems to indicate unmistakably that dissolved oxygen does play some rôle in the silver coulometer, but just how is not yet clear. Lewis[18] has determined the dissociation pressure of silver oxide through a con-

[18] G. N. Lewis, J. Am. Chem. Soc., 28 (1906), p. 139.

siderable range of temperature, and extrapolating his results, found that at 25° the pressure is less than 1 mm. It seems, then, that silver would tend to oxidize in the air at room temperature, but, of course, under ordinary conditions the rate is immeasurably slow. In contact with a solution of one of its salts, however, the action might go at an appreciable rate.

Some experiments performed in the early part of this work, when the question of the solubility of silver in silver nitrate solution arose, bear on this point. A loosely coiled spiral of sheet silver, having a total surface of 500 cm., was completely submerged in a 15 per cent. air-saturated, silver nitrate solution for six days. The silver was obtained from the United States mint. It was 99.98 per cent. pure, the impurities being gold, with possible traces of lead and copper. It had, of course, been carefully cleaned and heated for some time at a low red. Before placing in the solution, it weighed 83.14607 g., and at the termination of the test, after careful washing with distilled water and drying in vacuo, it weighed exactly the same, 83.14607 g. The silver was then suspended in an oxygen-saturated solution, and oxygen bubbled slowly through for three days. After this treatment it weighed 83.14629 g., a gain of 0.22 milligram, but this is almost too small to be significant. At any rate, these results serve to show that any action of an oxygen-containing silver nitrate solution upon metallic silver is too small to measurably affect the deposit when once formed in the coulometer.

It seems probable, however, that in passing from the ionic state to the crystalline metal the silver momentarily exists in some more active form which might readily be attacked by oxygen dissolved in the electrolyte. The existence of such a transition state is no new idea. If it be assumed, then, that a certain small amount of silver is oxidized in this way, and the oxide, or more probably, hydroxide, is retained by the deposit, one has an explanation of the observed phenomenon.

IX. The Purity of the Silver Deposit.

The suggestion just offered at once raises the old question of the purity of the silver deposited in the coulometer, a question which has received the attention of several investigators, but does not yet seem to be definitely settled. Rayleigh and

Sidgwick[2] (p. 429) made several analyses of deposits obtained in their electrochemical equivalent determinations which indicated the presence of impurity in the silver, but, as they pointed out, the method of analysis was not sufficiently exact to definitely settle the matter. They also heated several deposits for a short time at a low red, but obtained contradictory results, which left the existence of any contaminating substance quite uncertain. Richards, Collins and Heimrod[4] (p. 139) sought to determine whether or not the deposit from the Rayleigh form of coulometer contained included electrolyte by dissolving the silver in pure nitric acid, precipitating it as silver bromide, using atomic weight precautions and making use in their computation of the exact ratio, Ag : AgBr, obtained in the Harvard laboratory. The average of seven not very concordant experiments indicated the presence of .007 per cent. impurity.[19] In their later work, Richards and Heimrod abandoned the analytical method, and adopted a more direct one. The cathodes with deposits (from the porous-cup coulometer), after drying at 160° and weighing, were heated over an alcohol lamp to constant weight. The twelve experiments quoted unite in showing a loss on heating which is, on the average, .018 per cent. The authors regard this as convincing evidence that electrolyte is imprisoned in the deposited silver, and state that "the inclusion is probably chiefly in recesses of the platinum cathode."

Lastly, van Dijk[9] (pp. 262-267), following the method of Richards and Heimrod, just quoted, failed, in several cases, to find any loss when the deposit had been formed on a clean platinum cathode. When, however, the cathode was coated with a silver deposit from a previous experiment and heated to 500°, a deposit formed on this showed a very appreciable loss. This fact is of interest in the light of an observation made in the present work. It will be recalled that in two experiments (see Table II) in which a silver-coated cathode was used, duplicates showed a comparatively poor agreement. This seems to confirm, in a measure, van Dijk's conclusion that when silver is deposited on previously-heated silver, an inclusion of electrolyte may take place. Further experiments, however, led him to make the general statement that under the usual

[19] van Dijk[9] (p. 262) has called attention to an error in the computation of this result, which, when corrected, gives an average of 0.006 per cent.

method of treatment no solution is included by deposits from the porous-cup coulometer, and they are therefore to be regarded as pure silver. This is in flat contradiction of the conclusion of Richards and Heimrod, and it would appear that the whole question is in a decidedly chaotic condition.

The difficulty seems to be that the methods employed so far in examining the deposited silver are too indeterminate. Take, for example, the method of direct heating. If a loss of weight is observed, unless special precautions have been taken, there is bound to be some uncertainty as to just how this loss is to be distributed between the platinum dish and the silver deposit. Further, the method does gives not the slightest indication as to whether the impurity is all in the silver, or, as has been

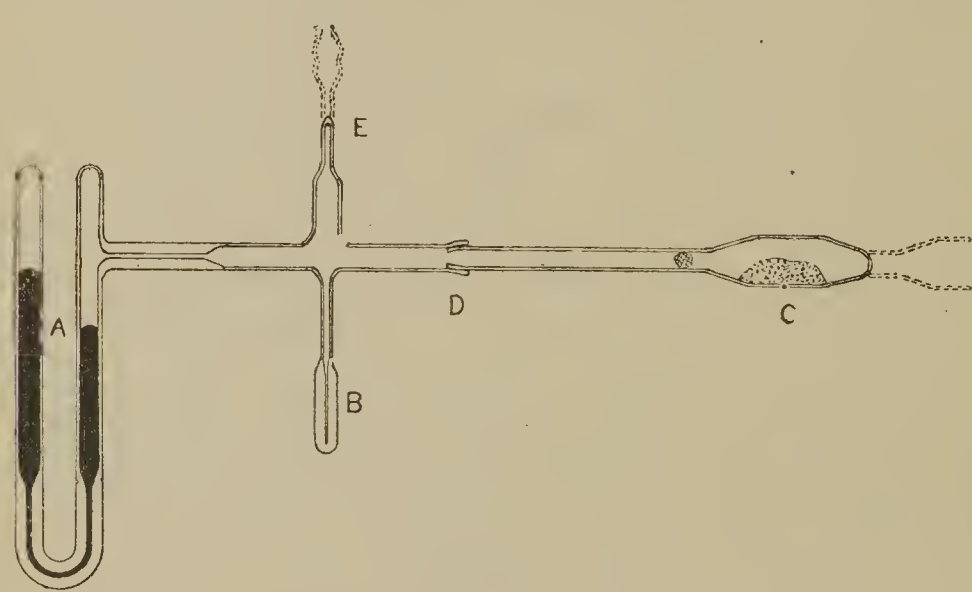


Fig. 3.

suggested, largely trapped in recesses of the cathode. Furthermore, the question as to the exact nature of the contaminating substance, which is of particular interest in this work, remains quite unanswered. It has very reasonably been supposed to be included electrolyte, but there is no direct proof of this. The analytical method, in addition to being inexact and tedious, is open to these same objections.

What is desired, then, is a method which will give information not only in regard to the quantity and distribution of any impurity, but also as to its constitution. This has been partially attained with the aid of the apparatus shown in section in Fig. 3. Referring to the sketch, (a) is a well-boiled out mercury manometer, (b) a short section of very uniform thermometer capillary,

and (c) a bulb of combustion tubing connecting by a ground joint (d) with the remainder of the apparatus. The dotted lines indicate the condition of the apparatus before the preparation for an experiment has been made.

Briefly, the plan was this: The silver under examination was sealed in the hard glass bulb, which was then joined to the manometer, and the whole thing evacuated. The bulb was then heated, pressure changes were observed, and any liquid distillate condensed in the capillary, which was subsequently sealed off. The experiments with this apparatus showed that on heating, both water vapor and a mixture of gases are given off by the silver. More in detail they were carried out as follows:

A deposit to be tested was carefully scraped from the cathode with a scrupulously clean platinum spatula. It came off cleanly, and the minute crystals of silver did not cohere. In this and all subsequent handling, every care was taken to avoid contamination. Next, the hard glass bulb and tube were cleaned and dried, a plug of freshly-glossed asbestos inserted in the neck, and the bulb heated to incipient redness. As soon as it cooled, the silver was introduced through the large end (shown by the dotted lines), and the constricted part sealed as shown. The apparatus was then put together, and the ground joint made tight with a minute quantity of marine glue. Connection with a mercury pump was made through the side tube (e) and the apparatus was evacuated to less than one millimeter pressure. Air was then slowly admitted through a phosphorus pentoxide tube, and the operation repeated several times, to eliminate any superficial moisture. Finally, the evacuation was carried to a small fraction of one millimeter, and the side tube (e) sealed off.

For heating, the bulb, together with a thermo-couple, was placed in a short section of asbestos-lined combustion tubing. A large Bunsen burner supplied the heat, and the free use of asbestos secured a uniform temperature throughout the bulb, and at the same time screened the remainder of the apparatus. The temperature in the eight to ten hours usually consumed by each test was raised in three or four steps to 600°-658°. During this period, it was frequently observed, and simultaneously the manometer reading and the temperature of the cool part of the apparatus were noted.

Almost from the commencement of the heating, the pressure within began to increase. At intervals, the capillary was cooled for a short time either by ice or a freezing mixture of ice and hydrated calcium chloride. This condensed the moisture, and so permitted one to judge approximately of its quantity, and also, from the pressure, of the quantity of gas liberated. One to two hours above 600° sufficed to bring conditions within to a state of equilibrium, and after some further heating, the capillary was cooled to —25° to —30° in the freezing mixture. When the cessation of pressure decrease indicated that all condensation of water vapor was at an end, the neck of the capillary was sealed. The bulb was then heated about one-half hour longer at 650°, in order to test the thoroughness of the previous treatment, but in no case was any appreciable change produced.

The water column sealed in the capillary was measured with the micrometer attachment of a microscope, and its mass computed. The final manometer reading, the temperature and the dimensions of the apparatus permitted a close approximation to the volume of gas contained.

In addition to the deposits from the porous-cup coulometer in air and in vacuo, one from a Rayleigh form of filter-paper coulometer was examined. This had been operated in series with the other two in Experiment 12. The deposit in it was 5.0462 g., and in the standard porous-cup instrument, 5.04563, the difference being .57 mg., which is smaller than the average, but, of course, varies widely with the exact dimensions of the filter-paper instrument (see van Dijk,[9] pp. 269-278). The results of all these tests follow:

Table V.

Tests of Silver Deposits.

No. of Test.	Source of Silv.	Mass of Silver.	Time at 600°+	Vol. of Gas at St. Cond.	Vol. Gas Per Gram St. Cond.	Mass of Water.	Per Cent. of Water in Deposit.
				Deposits from Porous-Cup Coulometer in Air.			
	Ex. No.	Grams.	Hrs.	c.c.	c.c.	mg.	
1	7	15	2	0.20	0.013	1.23	0.0082
2	8	10	2	0.11	0.011	0.97	0.0097
3	9	5	2	0.051	0.010	0.49	0.0098
4	11	5	3	0 054	0.011	. . . .	. . . . .
5	12	5	6	0.051	0.010	0.49	0.0098
			Mean		0.011		0.0094
				Deposits from Porous-Cup Coulometer in Vacuo.			
6	9	5	4	0.050	0.010	0.23	0.0046
7	11	5	3	0.034	0.007	0.29	0.0058
8	12	5	4	0.037	0.007	0.29	0.0058
			Mean		0.008		0.0054
				Deposits from Filter-Paper Coulometer (Rayleigh Form) in Air.			
9	12	5	6	0.054	0.011	0.47	0.0094

In the first test, the capillary tube was very long and narrow. For this reason, the condensation of water was very slow, and quite possibly not complete. This may explain the apparent large quantity of gas and smaller mass of water.

Before discussing the results, one further experiment may be mentioned. In order to determine whether some impurity still remained in the silver after heating at 600°, that from test 5 was removed from the bulb, crushed in a clean agate mortar, and placed in a quartz tube sealed at one end. This tube replaced the hard glass bulb in the usual apparatus. The silver was heated above the melting point, and in fusing gave evidence, by slight ebullition, of the escape of gas. The pressure within rose to 10 millimeters, but on cooling the quartz tube cracked,

so that the contents of the apparatus could not be examined. It appears, then, that treatment at 600° does not entirely remove the impurity, but the quantity of residual foreign matter is small. If, for example, it was water, the 10 millimeters pressure would have been produced by .05 milligram.

Turning now to the results of these tests, what answer do they give to the several phases of the problem stated at the beginning of this particular discussion? In the first place, they prove that the silver deposited in the coulometer from a *pure* water solution of silver nitrate does contain impurities which remain after drying the deposit in vacuo or, as usual, at 160°. These impurities, moreover, cannot be completely decomposed or set free below a red heat, and perhaps not without fusion of the metal. This is believed to be the first *direct* evidence of this fact, and now seems quite incontrovertible. It is probable that the low pressure within the apparatus materially aided the escape of the various gases, and that similar heating of the silver in air would not be so effective. Obviously, the usual manner of drying the deposited silver at 160° is in no wise effective in eliminating the included matter, and for the reasons mentioned before, the method of vacuum drying is to be preferred.

These tests, secondly, give some indication as to the nature of the impurity. This may be judged only by an examination of the decomposition products. The water from several experiments was tested carefully with methyl orange, and appeared perfectly neutral. As far as could be judged, it was pure. The gas from the 10 g. of silver, in test 2, was transferred, with the aid of a mercury pump, to a scrupulously clean gas burette containing purified mercury. The quantity of gas, .11 c.c., was, of course, very small, but every care was exercised in handling it, and any in-leaking of air was positively precluded. With the gas under somewhat diminished pressure, two drops of nearly colorless and strongly alkaline pyrogallol were run into the burette. At least, nine-tenths of the gas was at once absorbed simultaneously with a distinct darkening of the solution. This would indicate that the gas was largely oxygen, with perhaps oxides of nitrogen, the unabsorbed residue being, no doubt, nitrogen. The gas from test 6 was transferred to a tube for the production of gas spectra, and under spectroscopic

examination was found to contain nitrogen, with traces of hydrogen (water vapor). This would all indicate that water and silver nitrate were present in both the vacuum and air deposits, and the existence of silver oxide (or hydroxide) in the air deposit is undetermined.

Taking up now the quantitative side of the question, an inspection of the table reveals the fact that deposits formed under the same conditions yield approximately constant amounts of water and gas, and, what is of particular interest in the present work, that distinctly more (almost twice as much) of both were obtained from the deposit in air. Considering the fact that any uncondensed water vapor would be measured as gas, the concordance of results, in regard to this latter, is about all that could be expected, but any calculation made from these must be attended with some uncertainty.

Assuming, however, that the gas is all derived from the decomposition of silver nitrate, and assigning to it the least density which a gas so formed might have, *i. e.*, that of a mixture of oxygen and nitrogen, its mean per cent., by weight, from the air deposits would be about .0015. The water corresponding was on the average, .0094 per cent. Hence, the total matter expelled at 600° formed .011 per cent. of the deposit. The previously quoted result of Richards and Heimrod was .018 per cent. It is possible that the larger value was due to some inclusion between the deposit and the cathode, but the tests show that, contrary to the opinion of these authors, the greater quantity of impurity is contained in the silver itself. However this may be, the difference between the two results is not surprising, for in all probability the amount of impurity would be influenced by the conditions under which the deposit was formed. For the deposits in vacuo, the total substance set free represented .0065 per cent. of the silver, a little more than half that for the air deposits.

So far, the substances obtained *from* the silver have been mainly considered, and it is of interest to examine in some detail the exact nature and distribution of the impurity as it exists originally in the silver. In this way, some information as to the mode of inclusion may perhaps be gained.

In regard to the question of distribution, a phenomenon

observed in the execution of the several tests possesses some significance. In every case during the heating of the silver, it was observed that each increase in temperature produced a corresponding rise in pressure, which soon, however, attained a new fixed value, and continued almost unchanged so long as the temperature remained constant. This indicates, since the water present was not sufficient to saturate the gas space, that at each temperature a definite quantity of gas and water vapor

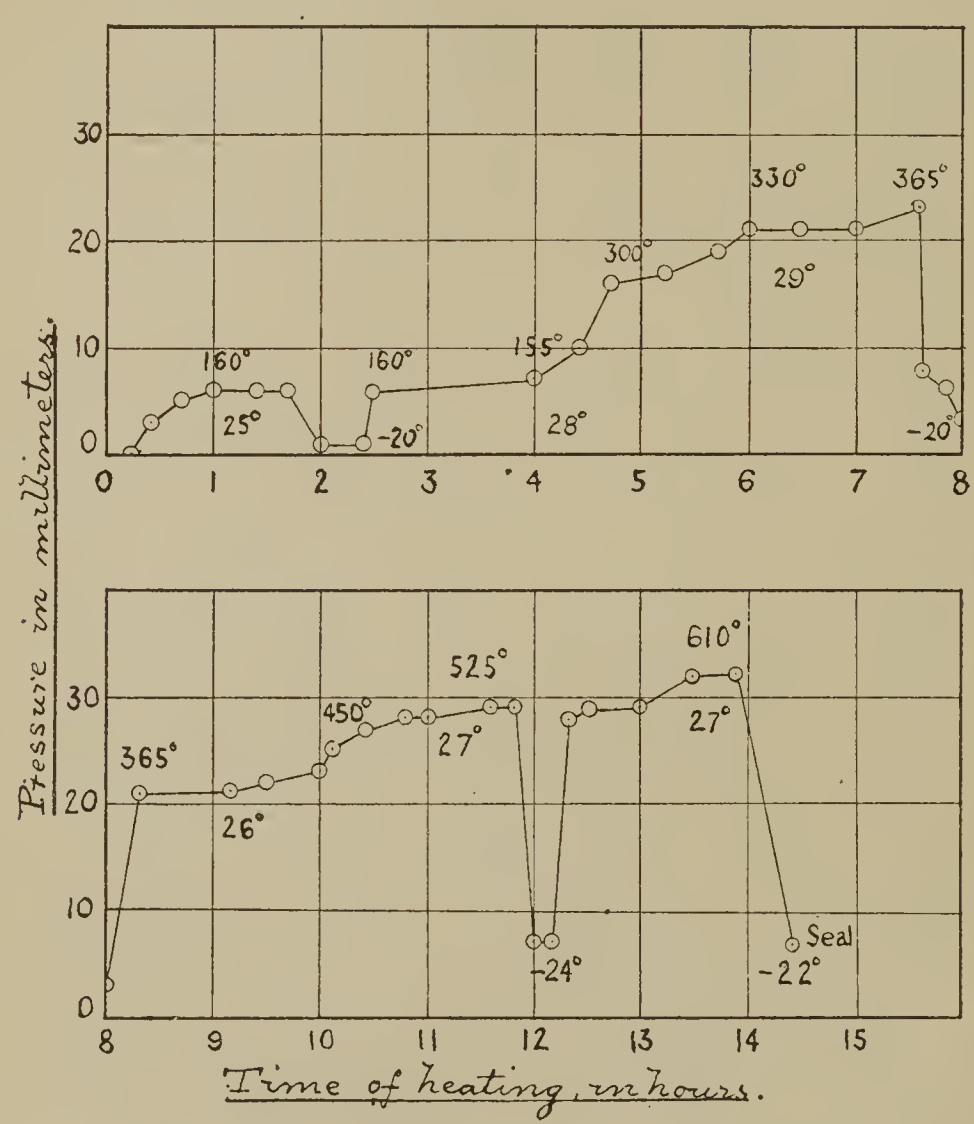


FIG. 4.

was in a short time eliminated from the silver, and thereafter almost no further change occurred until a further increase of temperature was made. This observation applied equally to deposits formed in air and in vacuo, and a pressure chart from a single test will perhaps make the point more clear. Fig. 4, with the exception that the experiment was more prolonged than usual, shows a typical one. Time of heating in hours is indicated by the abscissas, and pressure in millimeters by the

ordinates. The numbers above the graph give the temperature of the bulb containing the silver, and those below of the capillary side tube in which the water was condensed. This latter temperature, except at special times, applies to the entire apparatus, excluding the bulb. The heating at 160° apparently expelled only water, since, on cooling the capillary to —20°, the pressure corresponded very nearly to the vapor pressure of water at that temperature, and evidence of the formation of gas first appears after heating at 365°. In general, gas was first found at about 300°, which is approximately the temperature at which the decomposition of silver nitrate begins. Perhaps the most simple and satisfactory interpretation which may be assigned to these facts is that the impurity is distributed quite uniformly throughout the silver, and that thus the pressure, hence, temperature, necessary for the escape of the volatile constituents from any particular region is proportional to its distance from the surface of the particle.

The next point arising for consideration is the exact nature and source of the included matter. Other investigators have made the very natural assumption that it is mother liquor, that is, water and silver nitrate, and this has been so far assumed in the present discussion. Following up this idea for a moment, it is possible to calculate from the mass of gas obtained from a deposit the amount of silver nitrate it contained. Taking first the deposits in air, the minimum value for the mass of gas was previously (p. 285) shown to be .015 milligram per gram, which corresponds to .041 milligram of silver nitrate. The electrolyte used was invariably a 15 per cent. solution, hence this mass of salt would have been contained in .23 milligrams of water. The water actually obtained from 1 gram of silver was only .094 milligram, less than half, a result which is somewhat perplexing. This does not take into account the residue in the silver after the final heating at 600°, which, however, is too small to be of much importance. One explanation which suggests itself is that the previous drying of the deposit might remove some of the water, leaving behind the silver nitrate. This may be true to some extent, but with the included matter distributed uniformly through the silver, as it appears to be, it is hard to believe that more than half the water could be so

removed. If the silver had been precipitated by some purely chemical reaction, one would expect that, due to surface absorption, the included solution would have a concentration slightly greater than the average mother liquor, but the layer of electrolyte next to the cathode during electrolysis is surely no more, and probably distinctly less, concentrated than the body of solution. Evidently, then, either the residual matter is not all silver nitrate, or, if it is, it is retained other than by simple inclusion of electrolyte. This might all be beautifully explained by assuming that the deposit from the air-saturated solution contained silver oxide, more or less hydrated, with perhaps a small quantity of silver nitrate, and this, it will be recalled, is precisely what it was hoped to prove. Unfortunately, however, the ratio of gas to water obtained from the vacuum deposit where oxidation is out of the question, is slightly greater than the other, and here this explanation entirely fails.

Falling back, then, on the other possibility, that the included matter is *other* than simply trapped electrolyte, this idea finds support, first, in the constancy of the quantity of impurity in deposits formed under the same conditions, and second, in its apparently uniform distribution throughout the silver crystals, for it seems hardly probable that mere accidental inclusions of mother liquor would show such regularity. Recent developments of the solution theory indicate that there is some interaction between solvent and solute, for example, an association of solvent molecules about the particles of solute. Without going elaborately into the matter, it seems within reason to suppose that part, at least, of the included matter is carried into the deposit, associated in some definite way with the silver ions. Some idea such as this would form a basis for a far more scientific explanation of the presence of impurities in the silver than could ever be developed from the assumption of mere accidental inclusion of mother liquor.

It does not seem possible, with the facts at present at command, to give a complete and satisfactory explanation of the phenomenon. Already this discussion has been protracted almost more than the acutal experimental work warrants, and this rather detailed examination of the question has been given partly with the hope that it may serve to suggest future work, which is manifestly much needed along this line.

X. Partial Explanation of the Vacuum Effect.

Reverting now to the original question which occasioned this discussion, "how is the lighter deposit in vacuo to be explained?" it appears at once that part of the difference between the deposits can be accounted for by the unequal amounts of impurity included by them. Just why there should be more included matter in the air deposit has not yet been explained. The idea that part of it might be silver oxide (or hydroxide) arising from the action of the dissolved oxygen on the silver was untenable, but before leaving the subject, one more suggestion might be made.

It is a well-known fact that the presence in the electrolyte of substances which are not themselves altered by the flow of current may exert a marked influence on the nature of the deposit. As was stated before, the deposits in air and in vacuo appeared to the unaided eye quite similar, but it is possible that the dissolved air did affect the electrolytic reaction, in some way assisting the inclusion, accidental or otherwise, of a greater quantity of impurity. The one trustworthy experiment with a nitrogen-saturated solution (Exp. 14, Table IV) points to the oxygen alone as the cause of the irregularity, but it is not proper to put very much weight on a single experiment. About the most which can be done now is to state that a real difference does exist between the amounts of impurity included by deposits in air and in vacuo. The reason for this fact remains to be supplied by future investigation.

The most probable values for the total amounts of impurity in the deposits are as follows:

Deposits in Air.		Deposits in Vacuo.	
Water	0.0094 per cent.	Water	0.0054 per cent.
Silver nitrate	0.0041 " "	Silver nitrate	0.0030 " "
Total	0.0135 " "	Total	0.0084 " "

Difference, 0.0051 per cent.

The exact magnitude of the actual difference in mass between the deposits in air and in vacuo (see Table III) is a trifle uncertain, but is at least .007 to .008 per cent., which leaves .002 to .003 per cent. unaccounted for. Whether this difference

is due to some undetected impurity or to a real difference in the amounts of silver deposited in the two cases cannot be decided now, and further experimental evidence along the lines indicated is required before an adequate discussion of the phenomenon can be given.

XI. Conclusion.

Glancing back for a moment over the work, it appears that part of the main question stated in the introduction has been answered. It has been shown that the deposit from a water solution of pure silver nitrate free from air and in vacuo is distinctly lighter than one formed in air. This fact, supported as it is by two quite different, but concordant, pieces of evidence, namely, the directly determined difference in mass of the deposits and their different impurity content, seems indisputable. Results further indicate that saturating the solution with nitrogen produces the same effect as simply removing the air by evacuation.

In addition to the original problem, a quite important question arising in the course of the work, viz., that of the purity of the silver deposit, has been considered at some length. It has been definitely proved that silver deposited in the porous-cup coulometer, both in air and in vacuo, does contain a small, but in each case quite constant, quantity of impurity which is not removed by the usual method of treatment of the deposit. Further than this, evidence has been adduced to show that the impurity is not, as has always been assumed, simply included mother liquor.

One other point established by this investigation is worth repeating, namely, that *with proper care* the porous-cup silver coulometer is trustworthy to within 1 part in 100,000.

It is perhaps worth while to consider briefly the significance of the results so far obtained. The basal question underlying all investigation in this field is, "what is the true electrochemical equivalent of silver," and associated with it is the more general question, "what is the exact value of a Faraday in absolute units?" The electrochemical equivalent of silver is usually defined as the mass of that metal deposited by unit current in unit time. Evidently this is not, as van Dijk[9] (p. 268) asserts, the mass of the deposit obtained by the passage of this

quantity of electricity through a pure air-saturated silver nitrate solution. Further no coulometer has yet been devised which will give, without rather elaborate and uncertain corrections, the *true* electrochemical equivalent of silver. Thus, the fundamental question stated above remains still unanswered.

The present research, as is frequently the case, has served largely to open up some hitherto unexplored territory in the domain of coulometer work and to add a few to the many problems already associated with the operation of the silver coulometer. It seems probable that a solution of these would not only increase the usefulness of this instrument, but what is more fundamental, would add much to the knowledge of the exact nature and mechanism of the phenomenon of electrolysis.

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DISCUSSION.

Mr. Carl Hering: It seems to me what might be called the previous electrochemical history of that platinum cathode becomes quite important. If, for instance, that same platinum electrode had been used as an anode in a sulphuric acid solution, it would be saturated with oxygen. As we know, it actually combines with oxygen and forms some compound; the chemists don't know what it is, but it is not platinum; it is a compound of platinum and oxygen. If you then deposit on the platinum some other metal, you are not plating a platinum electrode, but one which is a combination of oxygen and platinum. Some of the current may first reduce some of the oxygen before it deposits silver. This may play a very important part in such accurate tests as are described here.

I have raised this same point a number of times at these meetings, and have always expressed surprise why those who make such researches do not use some other metal which does not have this very objectionable property. I had occasion to use some electrodes during tests in which it was very important that no such

action should take place. I tried platinum and found it absolutely worthless. It gave absolutely unreliable results, due to these causes. I tried various other things, and finally used gold, with which I got very excellent results. It seems strange, therefore, that in such researches some other metal is not used in place of the platinum. I think that, unless there are some other objections, gold electrodes might do very well, because they would at least overcome that objection.

I was pleased to see that a porous cup was used. At the meeting of the Society a year ago, I read a short paper, showing that the microscope reveals that during electrolysis there may be an actual bodily conveyance of minute particles through the solution. This is different from the migration of the molecules. I suggested at that time that some of these very accurate tests made with a silver coulometer may give inaccurate results owing to the deposition of these molar particles; the use of a porous cup would prevent this. I believe our president stated that the origin of the excrescences on cathodes was always found to be a speck of some foreign materials; this may have been transported and deposited as I described.

Mr. L. H. Duschak: In regard to the gas occluded by the cathode, the possibility of its influence upon the results has been considered, particularly as an explanation of the so-called "vacuum effect," but I said nothing about it because it does not fit the facts and seems to have no bearing on the results so far obtained.

Mr. G. A. Hulett: Mr. Hering's point about the depolarization of the cathode is one which we are considering at present, as well as the use of a gold cup as cathode. Bose has already pointed out that in the silver coulometer a part of the current may go to the removing the oxygen dissolved in the platinum of the cathode; however, Rayleigh worked with different cathode areas, and within the experimental error of his work there was no difference in the weight of the silver deposited by a given current; now the occluded oxygen would be proportional to the platinum area and on a large scale more of the current would go to removing this oxygen, and correspondingly less to depositing silver than on a smaller platinum area. Rayleigh's results are not as accurate as those obtained at present, but serve to indicate

that very little of the current goes to removing oxygen from the platinum cathode. Further, the silver deposit does not cover the platinum surface, but grows from points in the form of crystals; grow larger, but our results show that the deposit on silver is much more variable than on clean platinum, and this would seem to speak against the occluded oxygen playing much of a rôle. Our object in this preliminary work was to get some thing reproducible as a reference for future work, and that we surely have in the deposit on clean platinum with the method we are using. We now have some quite definite information about the impurity in this deposit, and it is next in order to consider all the possible cathode reactions in order to know whether the current is doing any other work at the cathode than depositing univalent silver, and then it is hoped that a comparison of the coulometer with our standard cells will give us a very exact value of the electrochemical equivalent of silver.

A paper read by title at the Twelfth General Meeting of the American Electrochemical Society, in New York City, October 19, 1907; President C. F. Burgess in the chair.

ELECTROLYTIC AND CHEMICAL ACTION OF AMMONIUM PERSULPHATE ON METALS.

By J. W. Turrentine.

The analogy between chemical and electrochemical reactions has been studied in considerable detail in this[1] and other laboratories and many data have been collected. Many reactions commonly considered and spoken of as purely chemical are in reality electrochemical. Still there is no sharp line of demarcation. Frequently reactions are induced by galvanic action, set up by bringing together in a corrosive medium, and in the presence of the compound with which a certain reaction is desired, two metals of differing electro-properties, so that an electric couple is formed. The zinc-copper couple of the "Gladstone and Tribe reaction" may be cited as an example of such a case. This is producing chemical action by a concealed, electrochemical reaction. We go a step farther and induce an electrochemical phenomenon in a purely chemical way—we can liberate ions which are generally set free only by electrolysis.[2]

When sulphate ions, SO_4'', are discharged electrolytically against a metallic anode they do one of three things—in cases where the anode is soluble they dissolve the anode quantitatively, forming sulphates; if the anode is insoluble and the current density low, oxygen is set free; or, if the current density is high and also the concentration of sulphate, the sulphate ions combine to form the divalent persulphate ion, S_2O_8''.

If we decompose the persulphate in the presence of an insoluble anode (or in the absence of any anode, which amounts to the same thing), we should expect the evolution of oxygen, and that we get. This may be shown by mixing, in a gas evolution bottle, concentrated sulphuric acid with a saturated solution of ammonium persulphate, containing an excess of persulphate crystals and a

[1] Bancroft, Trans. Am. Electrochem. Soc., 8, 33 (1905).

[2] Bancroft, Trans. Am. Electrochem. Soc., 8, 43 (1905).

small amount of manganous sulphate to act as catalytic agent and accelerate the reaction. An active evolution of oxygen ensues, a fact which may be demonstrated by bringing a glowing splint to the opening of the bottle. Since the addition of the sulphuric acid to the solution causes a rise in temperature, a thin glass bottle is the safest to use.

Again, if this liberation of sulphate ions is analogous to that produced by the electrolysis of a sulphate solution we should expect a soluble metal to be attacked, thus acting as an anode, and quantitative solution to take place.

COPPER.

To test this point a series of determinations were made in this laboratory of the solubility of pure, metallic copper as the ideal anode in a dilute, aqueous solution of ammonium persulphate, the consumption of persulphate being in each case also determined. The object of this paper is to present the results of these determinations. The method of procedure was simple and was as follows: A copper strip was bent into a spiral so that a large surface could be exposed in a small space. After having been cleaned and weighed it was placed in a beaker containing a solution of ammonium persulphate (10 c.c. of a standard solution containing 0.0829 grams per c.c. being added to 100 c.c. of water). This solution was stirred vigorously for an hour by a glass stirring rod attached to the axis of a small "Ajax" motor. At the end of the hour the strip was removed, washed, dried and weighed, and the loss in weight was noted. To the solution was then added a weighed amount of ferrous ammonium sulphate, 10 c.c. of concentrated sulphuric acid and 100 c.c. of boiling water.[3] It was then titrated rapidly with standard $KMnO_4$ solution. The excess of ferrous iron was calculated. Subtracting this value from the total iron added, gave the amount employed in reducing the unused persulphate. This in its turn subtracted from the total amount of persulphate gave the weight of that which had reacted with the copper. From this last value was calculated the equivalent weight of copper. A comparison was then made between the calculated and observed values. The following table gives the data on copper:

[3] Friend. Jour. Chem. Soc., 85, 1533 (1904).

	Total Persulphate.	Excess Persulphate.	Persulphate Used.	Cu Equiv.	Actual Cu Loss.
1	0.8293	0.0990	0.7303	0.2035	0.2050
2	0.8293	0.0258	0.8035	0.2240	0.2279
3	0.8293	0.0477	0.7817	0.2179	0.2185

The amount of persulphate which was not employed in dissolving the copper is indicated in the table by "excess" persulphate. The amount reduced by the copper is recorded under the head, "Persulphate Used." This weight of copper dissolved is equivalent to the action of a current of about 0.18 amp. for the same length of time.

It is seen that a varying excess of copper over that called for by the calculation is recorded. This excess loss could not be attributed to error in the analytical work, as all determinations of persulphate in the standardization of solutions were easily duplicated. The possibility of the solubility of copper in $(NH_4)_2SO_4$ in the presence of oxygen being suggested, a blank run with copper in neutral ammonium sulphate was made, with the result that it was seen that an average of 0.0025 gram was dissolved per hour in the ammonium sulphate. This would bring the results for copper easily within the limits of experimental error. The addition of ammonium hydroxide to the ammonium persulphate, it may be remarked, accelerates the rate of solution of the copper.

NICKEL.

Sulphate ions discharged electrolytically against a nickel anode normally dissolve nickel but slightly. Instead, oxygen is evolved. The presence of chlorides in the solution, it has been shown, causes corrosion and the formation of black nickelic oxide. Nickel anodes in ammonium persulphate, on the other hand, do dissolve to the sulphate. The results of two typical runs are given in the subjoined table:

	Total Persulphate.	Excess Persulphate.	Persulphate Used.	Ni Equiv.	Actual Ni Loss.
1	0.8293	0.2419	0.5874	0.1510	0.1326
2	0.8293	0.3510	0.4783	0.1230	0.1047

It may be observed that the solution of the nickel in the persulphate is not quite quantitative, there being a difference of about 13 per cent. between the actual loss due to the corrosion and the calculated nickel equivalent of the reduced sulphate. A slight evolution of oxygen may have occurred, but was not noticed. The nickel salt produced by the corrosion may act catalytically, as does manganese sulphate, to accelerate the decomposition of the persulphate. However, this point was not investigated, but attention was turned rather to the determination of the cause of the surprisingly large solubility of the nickel in the ammonium persulphate. Chlorides were sought for as a possible cause, but were found to be absent. As passivity of an anode is generally due to the formation on its surface of films of oxides or hydroxides, and as nickel hydroxide is known to be soluble in ammonia, it was deemed possible that the activity of the nickel anode in the persulphate was due to the presence of ammonium sulphate which dissolved the film of oxide that produced the passivity. Accordingly, to eliminate the influence of the ammonium salts, the solubility of nickel in sodium persulphate was determined, under conditions of temperature and concentration of solution similar to those whch obtained in the like experiment with ammonium persulphate. The slight loss in weight of 0.0005 gr. from a surface of about 20 sq. cm. was detected after an hour's stirring. This is in agreement with the electrolytic corrosion of nickel by sulphates, the presence of ammonium salts acting here as they do in the electrolysis to render the anode active—hence the use of the double sulphate of nickel and ammonium in the electrolytic purification and deposition of nickel.

Nickel, like copper, shows a slight solubility in neutral ammonium sulphate, 10-20 milligrams dissolving in an hour from an exposed surface of 20 sq. cm.

CADMIUM.

Cadmium, it was found, dissolves readily in ammonium persulphate without apparent evolution of gas. The calculated and observed values, however, do not agree. As the error gives the excess to the calculated rather than to the observed value, it cannot be explained, as was done in the case of copper, by the solubility of the metal in ammonium sulphate. The source of this discrepancy was not investigated.

ALUMINUM.

Aluminum as anode in the electrolysis of sulphates is but slightly corroded, due to the oxide films and consequent passivity. Furthermore, it tends to intercept the electric current by preventing the discharge of the anions. This phenomenon is made use of in the aluminum current-rectifiers. In ammonium persulphate solution only slight corrosion of the aluminum occurs, about 20 milligrams in one hour from a surface of 40 cm.^{2} exposed to corrosion; no oxygen is evolved. The analogy between the corrosion of aluminum in persulphate solution and as anode in sulphate solution seems to be complete.

IRON.

Iron anodes are dissolved by sulphate ions at low current densities, quantitative solution taking place. The valence assumed by the dissolved iron is that of the ferrous condition. In a solution of ammonium sulphate it reacts with the alkaline solution from the cathode region and precipitates as the slightly oxidized, green, ferrous hydroxide. At higher current densities, the rapid corrosion of the iron being prevented, oxygen is set free.

Ammonium persulphate acts on iron similarly and dissolves it to ferrous sulphate, thus upholding our analogy. The excess of ammonium persulphate reacts with the ferrous sulphate and oxidizes it, but only partially, to the ferric state. This is clearly shown by adding to the solution a known excess of ferrous ammonium sulphate and after following the prescribed procedure, titrating with permanganate. The presence of an amount of ferrous iron in excess of that added is indicated by the titration. The amount of the excess depends on the extent of the corrosion and on the temperature. In the case of our own experiments this condition was always shown, in one instance the ferrous iron in the solution in excess of that added to reduce the persulphate being equivalent to 0.80 grams of ferrous ammonium sulphate. The ferric sulphate formed readily hydrolyzes, precipitating ferric hydroxide. There is also a free evolution of gas which is not absorbed by alkaline pyrogallol and is also combustible in air. The origin of this gas must be either (1) from hydrogen set free by the action of acid in the solution on the iron, or (2) from

hydrogen dissolved in the iron,[4] (3) from the decomposition of carbides within the iron, evolving gaseous hydrocarbons, or (4) the breaking down of ferrous sulphate to ferric sulphate with the liberation of hydrogen, in a manner analogous to the decomposition of chromous salts.

The first explanation seemed quite improbable, as abundant ferric hydroxide formed in the solution, indicating, in spite of a slight acid reaction to litmus, a practically neutral solution. Furthermore, a piece of iron was allowed to stand without stirring in a solution of ammonium persulphate made alkaline with ammonia; the iron became covered with a deposit of ferric hydroxide. The evolution of gas was still noted. This made it seem extremely improbable that the liberation of gas was due to an acid solution.

If the gas was hydrogen dissolved in the iron, then the same should be got on making the iron an anode in ammonium sulphate. Accordingly, an iron anode thrust into an inverted burette with a parchment diaphragm surrounding the burette to prevent the diffusion of the cathode gases into the anode compartment, was dissolved by electrolysis in a neutral, 1 per cent. sulphate solution. A current density was used which would produce a slight evolution of oxygen at the anode. The cathode was of platinum. The gases evolved from the anode were collected in the burette and withdrawn for analysis. The results of four such runs are given in the following table:

	Total Volume.	Oxygen.	Hydrogen.
1	18.0 c.c.	12.2	5.8
2	32.5	26.2	6.3
3	16.0	12.6	3.4
4	18.0	13.0	5.0

More iron was dissolved in these experiments than was in the corrosion with ammonium persulphate, yet a smaller volume of hydrogen was obtained, so this explanation of the source of all the hydrogen had to be abandoned. The third point, the question of the formation of hydrocarbons, was tested by making an analysis of the gas by combustion in a Winkler-Dennis combus-

[4] Burgess, Trans. Am. Electrochem. Soc., 9, 197 (1906).

tion pipette. The total contraction in volume equaled the volume of gas taken for analysis plus one-half of its own volume—two volumes of gas combined with one of oxygen; this fact, coupled with the absence from the combustion products of carbon dioxide, showed the gas to have been only hydrogen.

If hyrogen is evolved by the transition of ferrous into ferric salts in ammonium persulphate solutions, the addition of ferrous salts should accelerate the reaction. Accordingly, two parallel runs were made by placing in 1 per cent. ammonium persulphate solution, in two breakers, iron strips in inverted burettes. To one solution was added two grams of ferrous sulphate. From the iron in pure persulphate were obtained 14.6 c.c. gas in 19 hours, and from the one to which had been added the ferrous salt 16.0 c.c. in the same time, showing a slight acceleration produced by the iron in spite of the decreased concentration of the persulphate due to its partial reduction by the ferrous sulphate. To make the concentration more nearly comparable a third run was made using a more concentrated solution of the persulphate; the ferrous sulphate was added by squirting it, in concentrated solution, through a tube against the face of the iron strip. A still greater acceleration was recorded in this case, 16.0 c.c. being evolved in 6 hours, as compared with the same evolved in 19 hours as observed in the case of one of the others. This clearly indicated that the acceleration was due to the increase in the concentration of the iron salts and not to that of the persulphate. It is doubtful if, in the last described experiment, there was any actual increase in the concentration of persulphate in the solution immediately surrounding the iron, as the ferrous sulphate was admitted directly against the iron and tended to displace the persulphate solution. While these phenomena were in accord with our theory, when attempts were made to determine what was acting as the catalytic agent to bring about this remarkable decomposition, it was noticed that iron in pure ferric sulphate solution, unstirred, also evolved hydrogen. Litmus showed such a solution to be acid. Alkaline hydroxides precipitated ferric hydroxide, but left the solution still acid. Ferrous sulphate and iron did not react to produce hydrogen; it is clearly impossible by definition for the reduction of ferric iron to be a reaction which evolves hydrogen; and as ferric sulphate hydrolyzes to produce free sul-

phuric acid, this acid seemed to be the source of the hydrogen. If this was true then the action of the alkaline ammonium persulphate had to be brought into agreement with it, so reversion was made to the persulphate. It has been mentioned above that the iron in the persulphate soon became incrusted with ferric hydroxide due to the solution of the iron in the persulphate to ferrous sulphate, the oxidation of a part of this to ferric sulphate and the precipitation of the ferric hydroxide by hydrolysis. A further solution of iron within the crust, even in the presence of free alkali in the solution, would lead to the production of ferric sulphate which, hydrolyzing, would leave an acid solution immediately surrounding the iron and would thus give rise to an evolution of hydrogen. Vigorous stirring from the beginning, on the other hand, should produce a film of hydroxide adherent and impermeable to the persulphate—should render the iron passive. This, it was found, it did. However, on standing in the solution unstirred, this film was broken through in spots and long threads of hydroxide grew out like roots from the iron. The evidence then seems to be in favor of our first explanation, however improbable it at first appeared. We feel sure that this is the true explanation of the phenomenon.

It may be suggested that the corrosion of iron in the presence of oxygen in many so-called neutral solutions is probably due to the free acid produced by the hydrolysis of ferric salts. The free acid may serve to carry the iron into solution as ferrous salt which is then oxidized by the air. The acid is regenerated by the hydrolysis of the resulting salt, just as in the commercial reduction of nitrobenzene to aniline, by means of the iron and hydrochloric acid, the acid is regenerated. While the acid is supposed to act catalytically, we know that it enters into the intermediate reactions.

SUMMARY.

(1) Sulphate ions are discharged when persulphates are decomposed in aqueous solution. These ions behave analogously to sulphate ions discharged electrolytically.

(2) Copper in ammonium persulphate behave just as does copper when employed as the anode in the electrolysis of sulphates.

(3) Nickel, cadmium and aluminum bear out the analogy be-

tween the chemical corrosion in ammonium persulphate and the electrolytic corrosion in ammonium sulphate.

(4) Iron is dissolved by persulphates. A portion of the dissolved iron subsequently appears as ferric sulphate, being oxidized by the persulphate in the solution.

(5) The free acid formed by the hydrolysis of ferric sulphate acts as a catalytic agent in the reaction between iron and water.

This work was suggested by Professor Bancroft and has been carried out under his direction. The author's thanks are due, and here expressed, to him.

Cornell University.

A paper read at the Twelfth General Meeting of the American Electrochemical Society, in New York City, October 19, 1907; President C. F. Burgess in the Chair.

THE ELECTROLYTIC DETERMINATION OF MINUTE QUANTITIES OF COPPER.

By E. E. Free.

The determination of quantities of copper less than one mgr. cannot be done satisfactorily by the ordinary procedure of electrolytic analysis because of the impossibility of weighing with sufficient accuracy the dishes or other cathodes usually employed. Phelps[1] avoids this difficulty by precipitating the copper electrolytically, dissolving the deposit and estimating it colorimetrically. By the use, however, of the electrode described

below, the colorimetric determination may be dispensed with and the copper weighed directly as deposited, a fair degree of accuracy being obtainable with quantities of copper as small as .05 milligram. The electrode is made from a small piece of platinum wire bent into a spiral with one end extending along its axis. It is supported in the bath by wrapping this free end

[1] Journal of Amer. Chem. Soc., 28, 368 (March, 1906).

four or five times about a hook of heavy platinum wire. If the hook be straight and slightly tapered toward the point the electrode may be easily attached and removed and makes perfect contact with the hook. The whole arrangement is shown in the figure. The electrode used by writer weighed about 0.3 gram.

The extraction and concentration of the copper are carried out by the usual methods. The electrolysis may be made in either nitric or sulphuric acid solution, low currents being used on account of the small cathode area. The writer uses 2 per cent. to 4 per cent. nitric acid and a few drops of sulphuric acid in about 25 c.c. solution and electrolyzes over night with about 1.8 volts and 0.01 ampere. The containing dish serves as anode. When the deposition is finished the electrolyte is washed out with a siphon or sucking-bottle without breaking the current. The electrode is grasped with a pair of small forceps, removed from the hook, washed successively in water, alcohol and ether, dried over sulphuric acid and weighed with great accuracy on a button balance. The copper is then removed by nitric acid and the electrode washed, dried and weighed as before. The difference gives the weight of the copper. Following are some results; the first four obtained by electrolyzing a solution of known strength, the last two by redissolving the copper from one precipitation and reprecipitating on another electrode.

No.	Copper Present (Mgs.)	Copper Found (Mgs.)
1	.529	.509
2	.492	.498
3	.556	.558
4	.499	.500

No.	Copper Found	
	1st precipitation Mgs.	2nd precipitation Mgs.
5	.092	.104
6	.348	.344

Uniformly good deposits are obtained from solutions containing nothing but copper salts and acids. If, however compounds of carbon or of platinum (derived from platinum dishes during the preliminary treatment) are present, the deposit will be black and loosely adherent owing to contamination with these elements and results high.[2] Organic matter dissolved in the disintegration

[2] The precipitation of carbon during electrolysis has recently been investigated by Blum & Smith. Proceedings Amer. Philosophical Soc., **46**, 60 (Jan.-Mar., 1907).

of a filter paper by nitric acid will in this way seriously interfere with the obtaining of good deposits. The difficulty may be avoided by making a preliminary (electrolytic) precipitation on a platinum dish in the usual way, dissolving the deposits and re-precipitating on the spiral electrode as above. The carbon and platinum remain undissolved on the first dish, and the electrolyte for the second precipitation is quite pure.

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A paper read by title at the Twelfth General Meeting of the American Electrochemical Society, in New York City, October 19, 1907; President C. F. Burgess in the chair.

THE TREATMENT OF STORAGE BATTERY ELEMENTS BEFORE PUTTING THEM OUT OF COMMISSION.

By O. W. Brown and R. R. Sayers.

The plates of storage battery elements of stationary cells are usually dried before they are shipped. Even the elements of vehicle cells must also be similarly treated when they are to be shipped a very great distance. The drying of the elements may lead to serious loss in capacity and efficiency, and may also considerably decrease the life of the battery, if the proper method of treatment accompanying the drying is not carried out. This process entails expense and endangers the life and capacity of the battery, and should be resorted to only when necessary for shipment or when a battery must be put out of commission for several months and cannot receive a monthly recharge. In order to avoid the expense and danger entailed in drying battery plates, many manufacturers ship their batteries unformed, and allow the buyer to form his own elements after they have been permanently installed. Much risk, however, is run in depending upon a person entirely unfamiliar with battery manufacture to form the elements in the proper manner.

Various methods of treatment are used and recommended for drying battery plates which are to be put out of commission. Even the larger and more experienced manufacturers of storage batteries do not seem to agree as to the best process of drying the plates. The treatment which will leave the plate in the best physical condition and with its original capacity is obviously the one to be used.

The writers have carried out comparative tests on methods of treatment which have occurred to them and also on those recommended by some of the leading manufacturers of storage batteries, and the results are here given.

A number of negative plates were prepared by pasting Pumpelly grids with a mixture of 900 grams of "glass makers'" red lead and 150 c.c. of 1.2 sp. gr. sulphuric acid. The grids were 4¾ inches wide, 7¾ inches long and about 3/16 inch thick, and weighed 340 grams each. About 400 grams of red lead were required for each plate. The paste was mixed very thoroughly before it was applied to the grids. The plates were allowed to dry forty-eight hours after pasting, after which they were hardened in 1.1 sp. gr. sulphuric acid and then dried at room temperature a second forty-eight hours.

Positive plates were prepared in the same manner as the negatives, except grids of the usual staggered form, weighing 320 grams each and which were 4⅞ inches wide, 7⅞ inches long by 5/32 inch thick, were used. Each of these grids required about 370 grams of red lead.

When the plates had dried forty-eight hours after being hardened, each one was placed between two hard rubber separators (5/32 inch thick) and on the outside of each separator was placed a dummy of sheet lead, which was followed by a glass plate. These elements were securely held together by strong rubber bands. The ribs on the separators were placed against the battery plate, instead of against the lead dummies, to insure good circulation of electrolyte at the surface of the plates during "forming." The glass plates on the outer side of the lead plate overcame any tendency of the plates to buckle. The lead dummies were of the same size as the battery plates, while the glass plates were ½ inch longer and ⅛ inch wider.

The elements were placed in 1.1 sp. gr. sulphuric acid and a current of 1.5 ampere (0.02 ampere per square inch) was passed through the cells until the negatives gave a cadmium reading below —0.1 volt and the positives above +2.3 volt. This required from seventy to eighty hours. (When the negative terminal of the voltmeter is connected to the plate which is being tested, the cadmium readings are marked —.) The cells were next discharged for fourteen hours at a 1.5-ampere rate, after which they were charged at the same rate.

The elements were then torn down, and the lead dummy plates replaced by battery plates. Each negative was set up between two positive plates, while each positive to be tested was set up between two negatives of the same size. The elements were now

placed in separate glass jars, each containing about 2,000 c.c. of 1.225 sp. gr. sulphuric acid, and were charged at a 3-ampere rate, after which they were discharged and charged at a 5-ampere rate for several times. Negatives giving a cadmium reading of —0.2 volt during charge were considered fully charged, while they were discharged to +0.25 volt. Positives were charged until their cadmium readings were +2.45 volts (while charging), and discharged to +2.00 volt cadmium. In all of the tests of the capacity of the plates, the elements were charged on one day, allowed to stand on open circuit over night, and then discharged. When the capacities of the plates were the same on successive discharges, they were fully charged; the different plates were subjected to the various methods of treatment and dried. After the plates had dried for several days, they were again assembled with battery plate dummies, placed in 1.225 acid and fully charged. The plates were then tested for capacity by repeated charge and discharge at the 5-ampere rate.

The following is a record of the treatment given each plate in order to put it out of commission, and the appearance of each before and after being put out of commission.

TREATMENT OF NEGATIVES.

No. 1 was taken from the acid, washed in distilled water, and then allowed to stand thirty hours in distilled water. It was next dried nine days, when it seemed thoroughly dry. It was somewhat lighter in color after drying than before and showed sulphation in some few places. As is shown by the table and curves given below, the capacity remained the same.

No. 2 was transferred to distilled water and discharged at a 3-ampere rate until it was, at last, short-circuited, and the voltage fell to zero. It was then dried nine days. It was some darker after being put out of commission than before, but was in good physical condition. The capacity remained unchanged.

No. 3 was simply taken from the acid and dried nine days. When taken out of acid, it had a good, dark color and was in excellent physical condition. It retained its color after drying, but was badly cracked and considerably sulphated. However, the capacity was not altered.

No. 4 was placed in a formalin solution (300 c.c. of 40 per cent. formalin to 2,100 c.c. distilled water) for thirty hours, and

then allowed to dry nine days. It seemed to have a few more cracks after drying than before, retained its color, and still held a slight amount of moisture. When tested, it possessed its original capacity.

No. 5 was put into distilled water, discharged at a 5-ampere rate until it was short-circuited and the voltage of the battery had fallen to zero. The physical condition of the plate was practically the same after as before treatment, except it was somewhat lighter in color. However, the plate lost considerably in capacity and could not be restored by repeated charge and discharge.

No. 6 was treated in the same manner as No. 5, except a formalin solution (300 c.c. 40 per cent. formalin to 2,100 c.c. distilled water) was substituted for distilled water. It remained in practically the same physical condition. The capacity was found to be somewhat less after treatment.

No. 7 was treated the same as No. 5, except it was allowed to remain in the 1.225 sp. gr. sulphuric acid, instead of being transferred to distilled water. It had the same physical appearance after drying as before, except it was slightly sulphated. It lost somewhat in capacity.

No. 8 was transferred to a 10 per cent. solution of potassium sulphate and treated the same as No. 5. The physical condition and capacity were the same, after treatment, as plate No. 7.

No. 9 was overcharged (to —0.24 Cd/Pb) and placed in the drying rack. After thirty minutes it began to steam, and was cooled in distilled water ten minutes. It was again put in the drying rack, and, after one hour, it was cooled ten minutes as before. It was not so warm this time. The above treatment was repeated, the plate being left in the rack two hours this time, after which it did not again heat. It was then dried fourteen days. This plate retained its good color and physical strength. The capacity was very slightly increased.

No. 10 was a duplicate of No. 9 and showed the same results.

No. 11 was put into distilled water and allowed to stand twelve hours. It was dried fourteen days, after which it had a slightly lighter color and a few more cracks than before. It gained slightly in capacity.

No. 12 was put in the drying rack. After thirty minutes it became steaming hot. It was cooled for ten minutes in distilled

water, replaced in the drying rack, and then cooled a second time for ten minutes in distilled water. After drying another hour and cooling for ten minutes as before, the plate was dried two hours, during which time it did not become warm. It was then put in 1,225 sp. gr. sulphuric acid for one hour, removed, and dried for nine days. It remained in excellent condition in every respect. The capacity was practically unchanged.

TREATMENT OF POSITIVES.

No. 1 was placed in distilled water for twelve hours, and was then allowed to dry nine days, at the end of which time it was in very good condition. The capacity was the same after treatment as before.

No. 2 was put in distilled water and discharged at a 3-ampere rate until the voltage fell to zero. After drying nine days, it seemed to possess very good strength, but was sulphated considerably. The capacity was unchanged.

No. 3 was overcharged ($+2.5$ Cd/PbO_2). It was then dried for about thirty minutes, until the negative dummies began to steam, when it was cooled in distilled water ten minutes. It was again dried until the negatives became heated, when it was cooled as before. After the third treatment in this manner, the negatives remained cool, and the positive was then allowed to dry nine days. The physical condition was not impaired and the capacity remained unchanged.

No. 4 was taken from the acid and dried nine days. It retained its good physical condition; however, for some reason unknown to the writers, the capacity increased.

No. 5 was overcharged ($+2.52$ Cd/PbO_2) and then given the same treatment as No. 3. When the negatives no longer became heated, the positive was placed in 1.225 sp. gr. sulphuric acid for one hour, after which it was dried nine days. This positive was in very good condition after drying, had a rich, dark brown color, and its capacity was slightly increased.

When the plates were put in commission, after being dried, they were charged twenty hours at 1½ amperes, and then the charging rate was increased to 5 amperes and the charge continued until the cadmium reading of each cell indicated that it was completely charged.

The capacity and efficiency of the plates before and after treatment are given in the table below. The curves representing the cadmium readings during charge and discharge are found immediately after the table.

Each plate was given about six discharges and charges before treatment and the same number after treatment; however, only the last two tests before and two of the tests after treatment are given in the table. The batteries were kept at about 25° C. while the tests were being made. The specific gravity of the electrolyte at the end of the discharge of each cell was usually about 1.200 while the acid was always adjusted to 1.225 sp. gr. before the discharge was started.

As was stated above, the charge and discharge rate was 5 amperes. The negatives were discharged until they read +0.25 volts against cadmium, while discharging at the 5-ampere rate, while the positives were discharged to +2 volts, cadmium.

NEGATIVE PLATES.

	BEFORE TREATMENT.						AFTER TREATMENT.					
	DISCHARGE.		CHARGE.				DISCHARGE.		CHARGE.			
	E. M. F. to Cd. at Beginning.	Ampere Hours.	E. M. F. to Cd. at Beginning.	E. M. F. to Cd. at End.	Ampere Hours.	Current Efficiency.	E. M. F. to Cd. at Beginning.	Ampere Hours.	E. M. F. to Cd. at Beginning.	E. M. F. to Cd. at End.	Ampere Hours.	Current Efficiency.
1	0.18	22.5	0.12	—0.18	26.25	85.7%	0.175	22.5	0.125	—0.20	27.5	81.8%
1	0.18	22.75	0.13	—0.18	25.00	91.0	0.18	22.5	0.125	—0.20	26.25	85.7
2	0.19	22.5	0.12	—0.18	26.25	85.7	0.18	22.91	0.14	—0.20	26.66	85.9
2	0.18	22.75	0.13	—0.19	25.00	91.0	0.18	21 25	0.135	—0.20	26.25	80.9
3	0.18	22.5	0.12	—0.18	27.5	81.8	0.175	22.50	0.125	—0.20	27.5	81.8
3	0.18	22.75	0.13	—0.18	25.00	91.0	0.18	22 50	0.125	—0.20	25.25	85.7
4	0.18	20 41	0.14	—0.18	25.83	79.0	0.18	21.66	0.14	—0.20	23.75	80.9
4	0.19	21.66	0.12	—0.18	27.5	78.7	0.18	21.25	0.133	—0.20	26.91	78.9
5	0.185	25.66	0.12	—0.20	25.83	99.1	0.18	23.75	0.13	—0.20	24.5	96.8
5	0.175	26.25	0.135	—0.20	28 33	92.8	0.19	23.00	0.135	—0.20	24.6	93.7
6	0.185	25.66	0.12	—0.20	25.83	99 1	0.18	23.75	0.137	—0.20	25.0	95.0
6	0 175	26.25	0.135	—0.20	27.66	94.8	0.195	23.00	0.13	—0.20	24.8	92.8
7	0.18	25.83	0.12	—0.20	25.83	100 0	0.18	24 16	0.13	—0.20	24.5	98.4
7	0.175	26.25	0.135	—0.20	28.33	92.8	0.19	23.50	0.135	—0.20	24.6	95.5
8	0.185	25.83	0.13	—0.20	25.83	100.0	0.18	23 53	0.13	—0.20	25.0	93.3
8	0.175	26.25	0.135	—0.20	28.96	91.0	0.195	23.33	0.13	—0.20	24.8	92.8
9	0.18	27.50	0.13	—0.20	28.33	92.8	0.18	28.00	0.13	—0.20	27.75	100.5
9	0.185	26.75	0.135	—0.20	26.25	100 0	0.175	26.00	0.13	—0.20	27.5	94.6
10	0.18	24.00	0.13	—0.20	25.75	93.0	0.180	26.00	0.13	—0.20	27.91	93.4
10	0.185	23.33	0.13	—0.20	25.00	93.3	0.18	26.00	0.13	—0.20	27.0	96.3
11	0.18	23.75	0.13	—0.20	24.00	99.0	0.175	29.66	0.14	—0.20	32.5	92.9
11	0.18	24.00	0.135	—0.20	25.75	93.25	0.175	30 58	0.14	—0.20	30 75	99.2
12	0.19	23.75	0 135	—0.20	26.00	91.5	0.175	25.25	0.14	—0.20	30.75	82.25
12	0.18	23.33	0.13	—0.20	24.33	89.6	0.18	24.75	0.135	—0.20	28.75	86.0

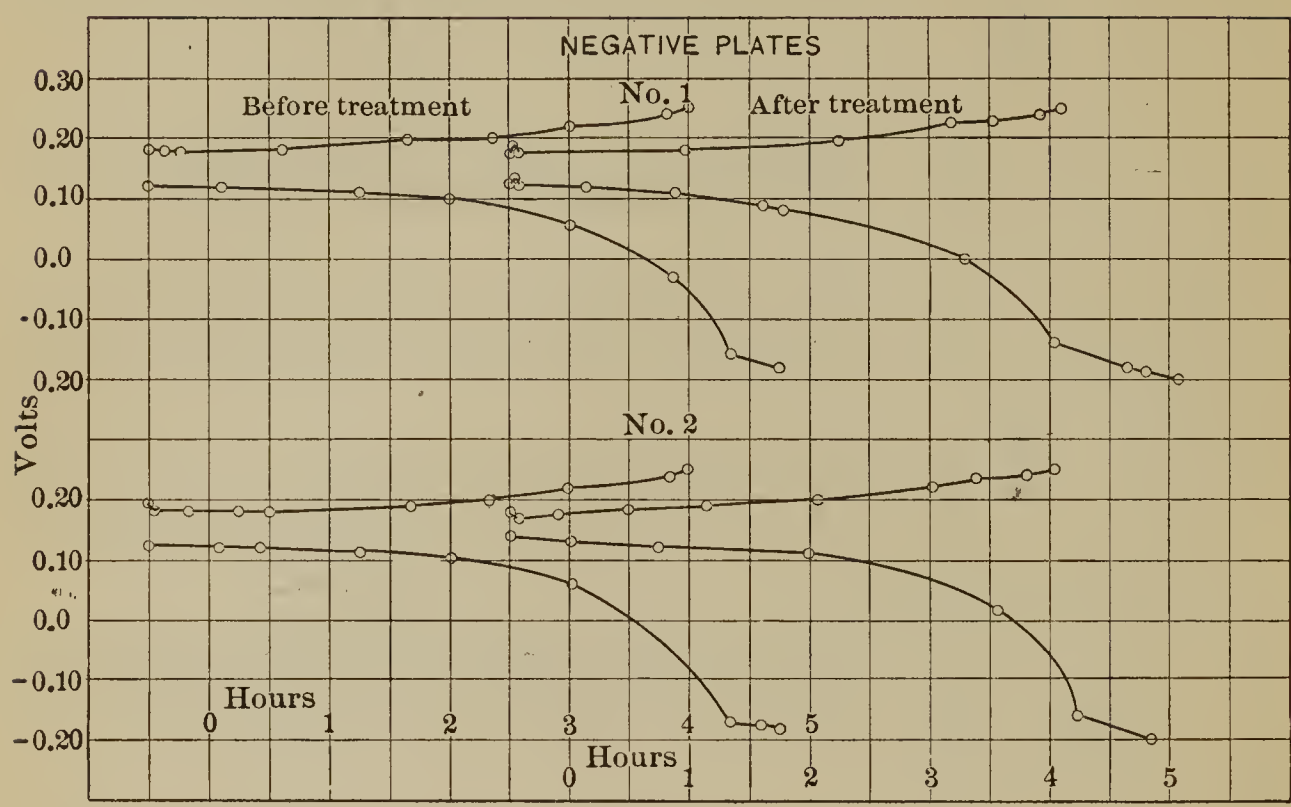
NEGATIVE PLATES
Before treatment
No. 1
After treatment
No. 2
Volts
0.30
0.20
0.10
0.0
-0.10
-0.20
Hours
0
1
2
3
4
5

FIG. 1.

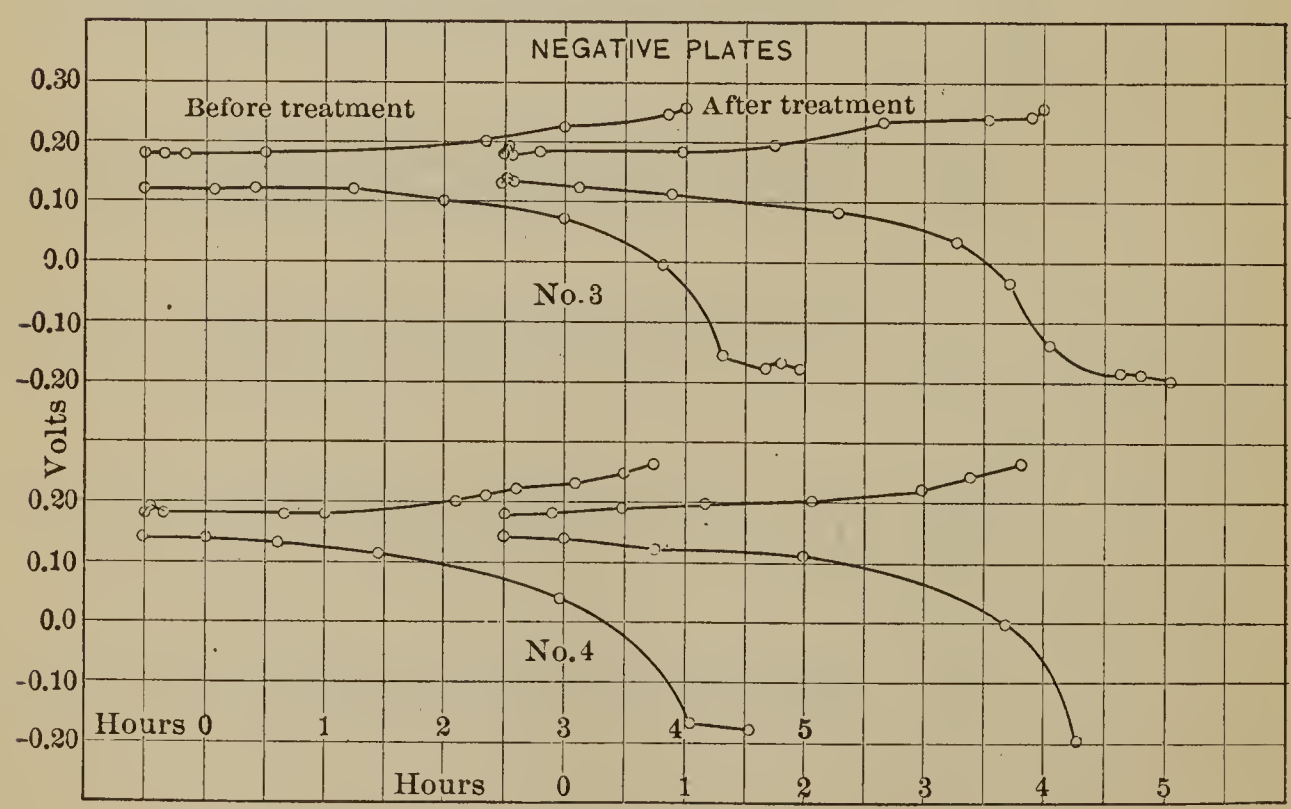
NEGATIVE PLATES
Before treatment
After treatment
No. 3
No. 4
Volts
0.30
0.20
0.10
0.0
-0.10
-0.20
Hours
0
1
2
3
4
5

FIG. 2.

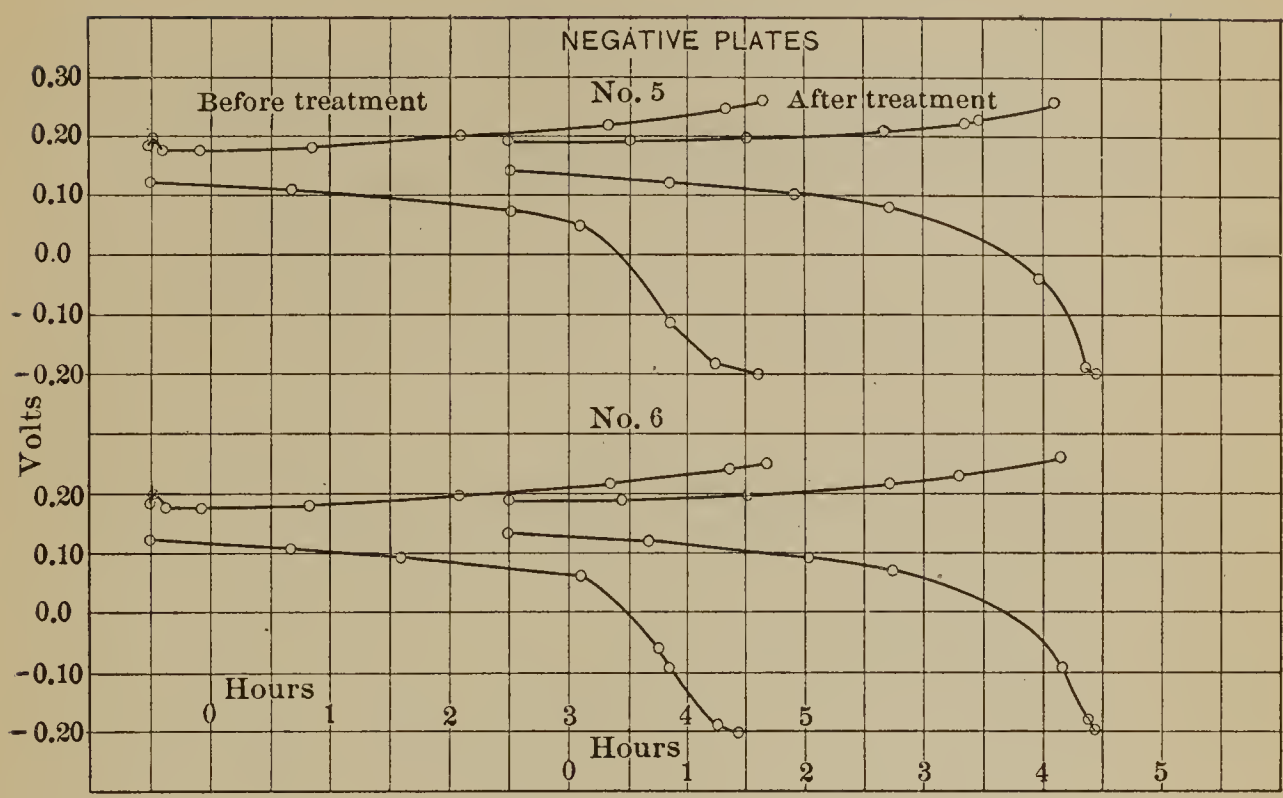
NEGATIVE PLATES
Before treatment
No. 5
After treatment
No. 6
Volts
0.30
0.20
0.10
0.0
- 0.10
- 0.20
Hours
0
1
2
3
4
5

FIG. 3.

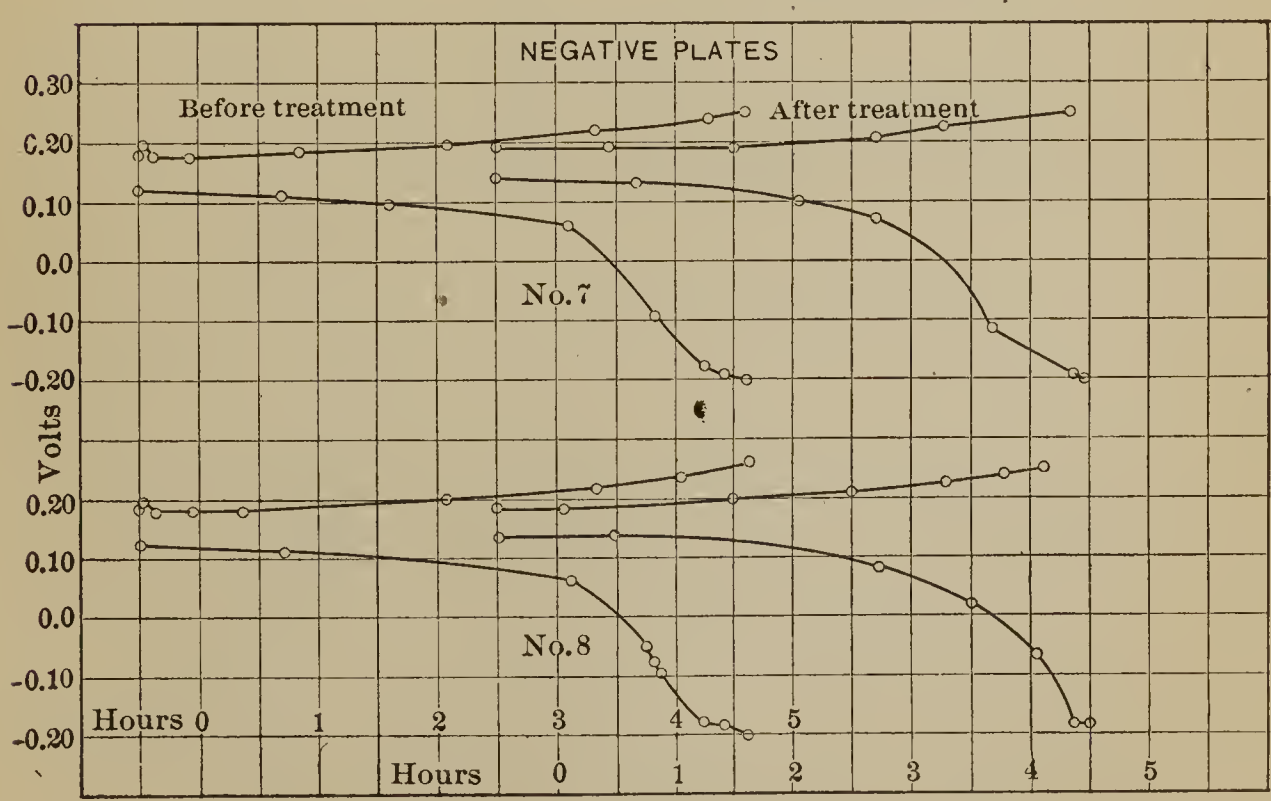
NEGATIVE PLATES
Before treatment
After treatment
No. 7
No. 8
Volts
0.30
0.20
0.10
0.0
-0.10
-0.20
Hours
0
1
2
3
4
5

FIG. 4.

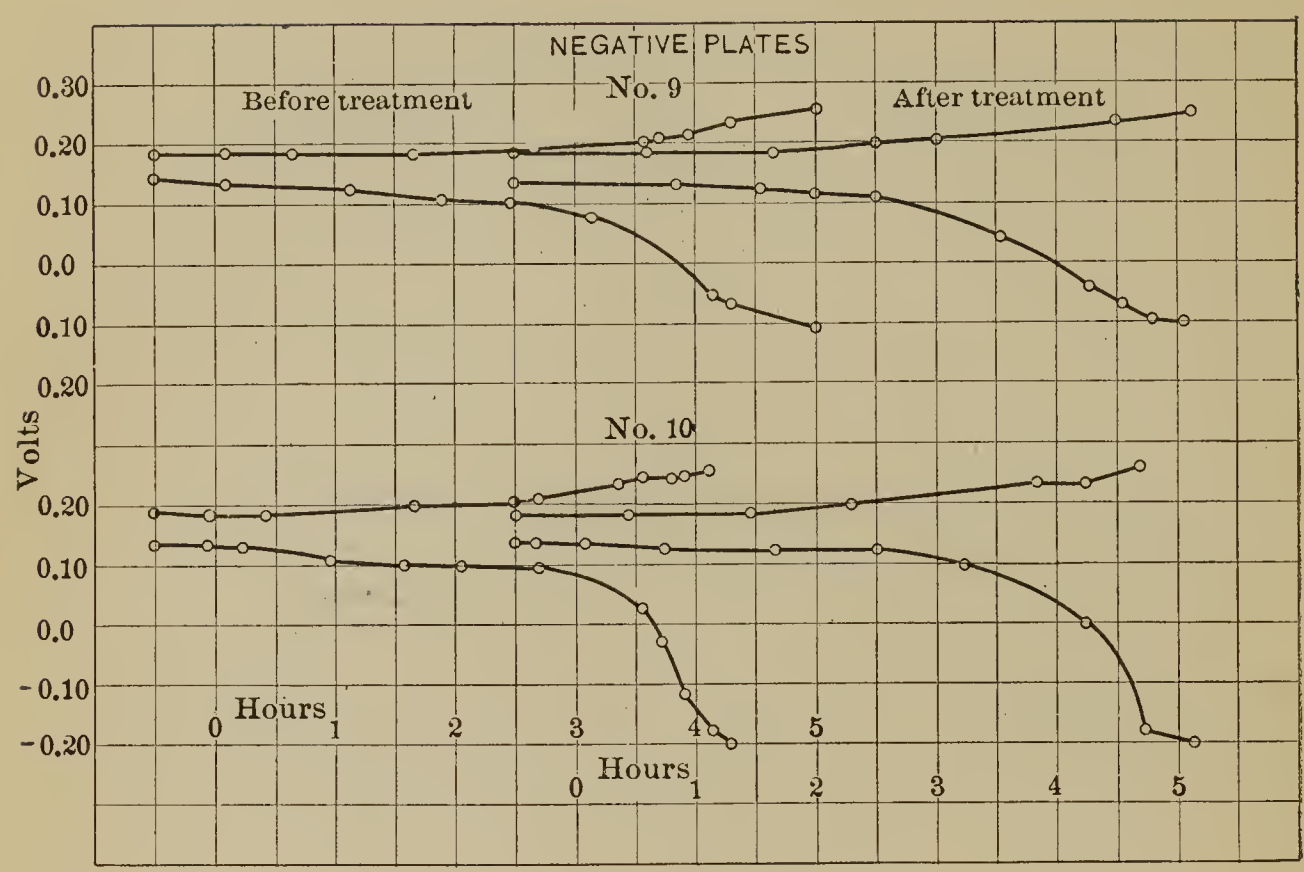
NEGATIVE PLATES
No. 9
Before treatment
After treatment
No. 10
Volts
0.30
0.20
0.10
0.0
0.10
0.20
0.20
0.10
0.0
-0.10
-0.20
Hours
0
1
2
3
4
5
Hours
0
1
2
3
4
5

FIG. 5.

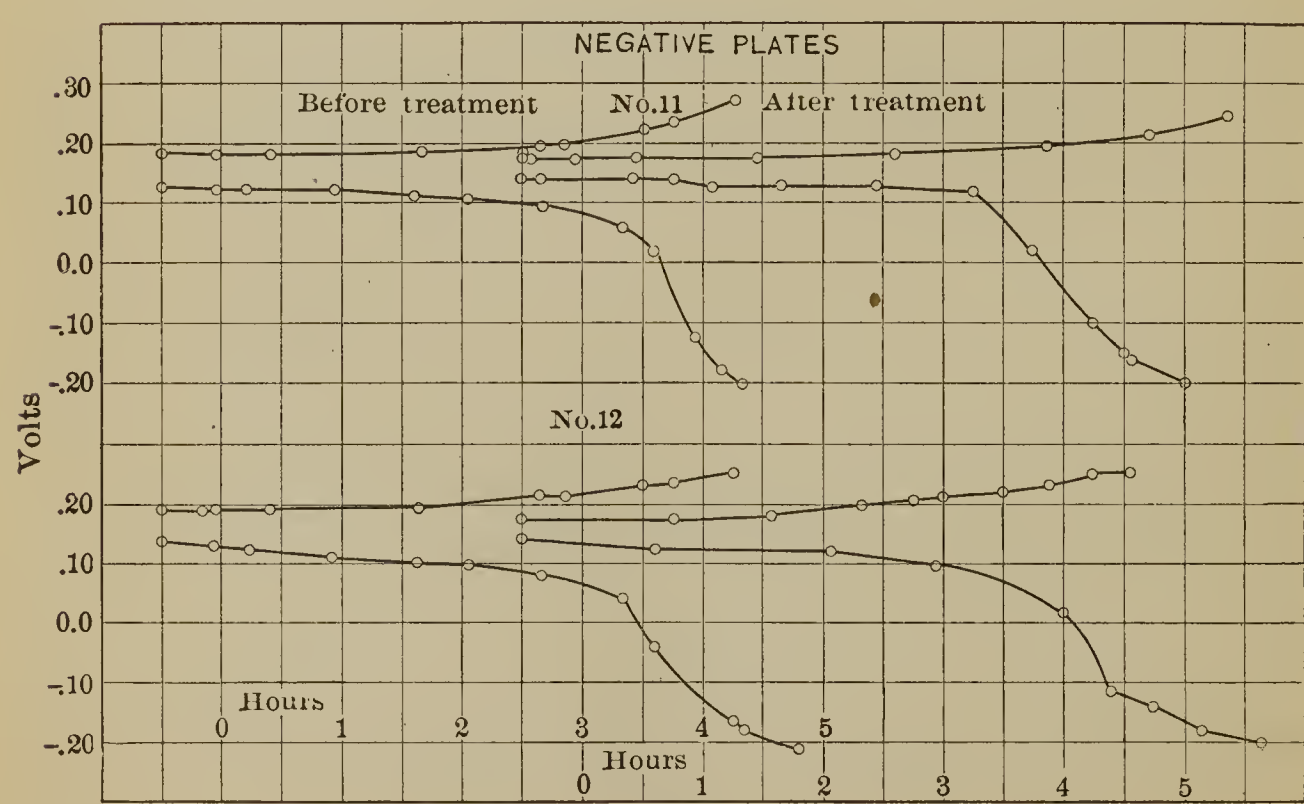
NEGATIVE PLATES
Before treatment
No.11
After treatment
No.12
Volts
.30
.20
.10
0.0
-.10
-.20
.20
.10
0.0
-.10
-.20
Hours
0
1
2
3
4
5
Hours
0
1
2
3
4
5

FIG. 6.

POSITIVE PLATES.

	BEFORE TREATMENT.						AFTER TREATMENT.					
	DISCHARGE.		CHARGE.			Current Efficiency.	DISCHARGE.		CHARGE.			Current Efficiency.
	E. M. F. to Cd. at Beginning.	Ampere Hours.	E. M. F. to Cd. at Beginning.	E. M. F. to Cd. at End.	Ampere Hours.		E. M. F. to Cd. at Beginning.	Ampere Hours.	E. M. F. to Cd. at Beginning.	E. M. F. to Cd. at End.	Ampere Hours.	
1	2.175	15 41	2.385	2.46	16.25	93.7%	2.17	15.75	2.40	2.455	16.25	96.8%
1	2.17	15.16	2.40	2.45	16.00	94.6	2.17	15.25	2.40	2.45	16.00	95.4
2	2.17	15.25	2.26	2.45	17.25	88.6	2.17	16.25	2.36	2.48	17.25	94.3
2	2.17	15.75	2.39	2.45	16.25	95.5	2.15	15.75	2.40	2.45	16.25	96.8
3	2.165	15.25	2.25	2.45	16.5	93.7	2.18	15.75	2.40	2.45	15 75	100.0
3	2.15	15.25	2.40	2.45	16.25	93.6	2.17	15.25	2.39	2.45	16.00	95.4
4	2.17	15.00	2.25	2.45	17.25	87.0	2.17	17.00	2.37	2.45	15.58	109 1
4	2.15	15.08	2.21	2.45	16.25	92.8	2.17	17.25	2.37	2.45	17.25	100.0
5	2.17	17.00	2.39	2.45	18.00	94.8	2.145	18.08	2.35	2.45	18.75	96.8
5	2.175	16.75	2 38	2.45	17.5	95.6	2.155	17.83	2.36	2.45	18.00	94.8

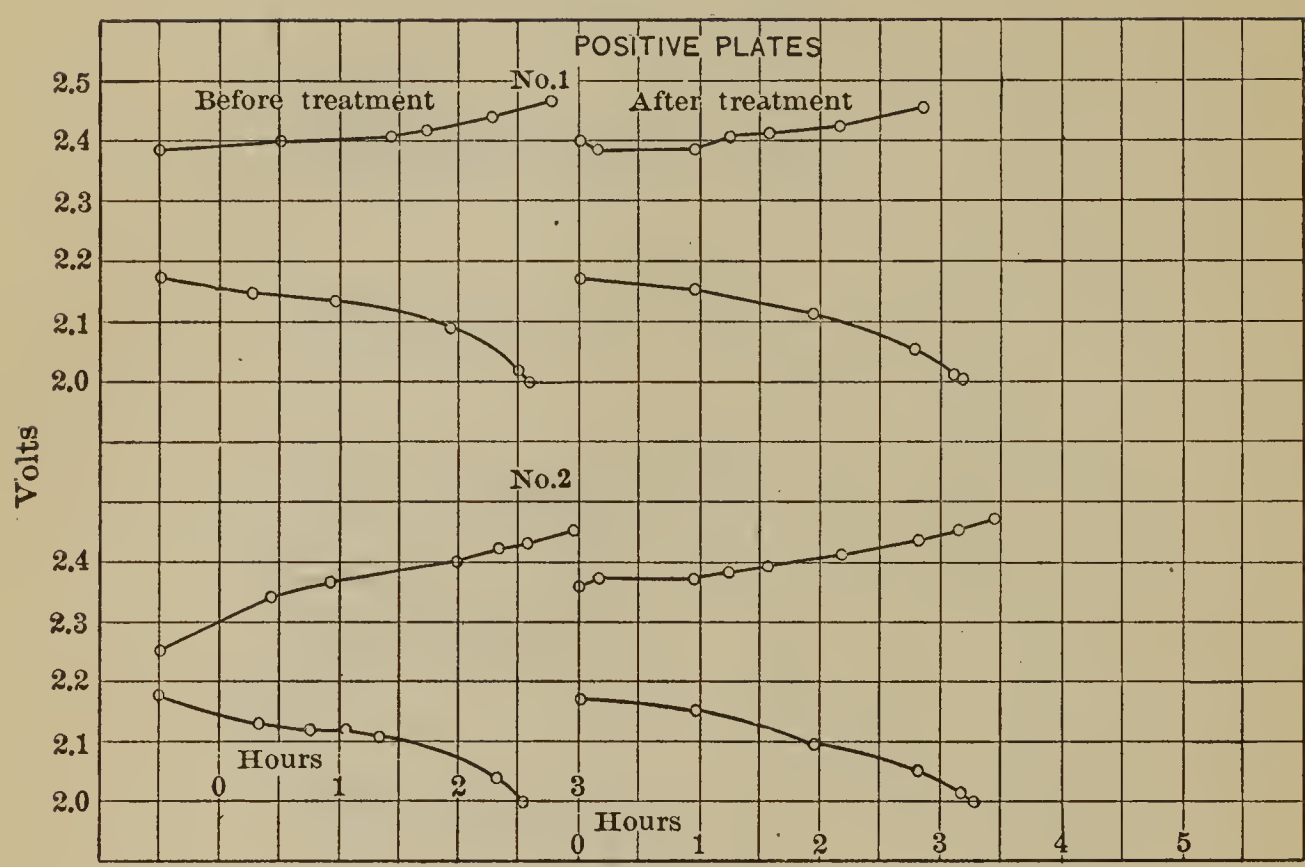
POSITIVE PLATES
No.1
Before treatment
After treatment
2.5
2.4
2.3
2.2
2.1
2.0
Volts
No.2
2.4
2.3
2.2
2.1
2.0
Hours
0
1
2
3
Hours
0
1
2
3
4
5

FIG. 7.

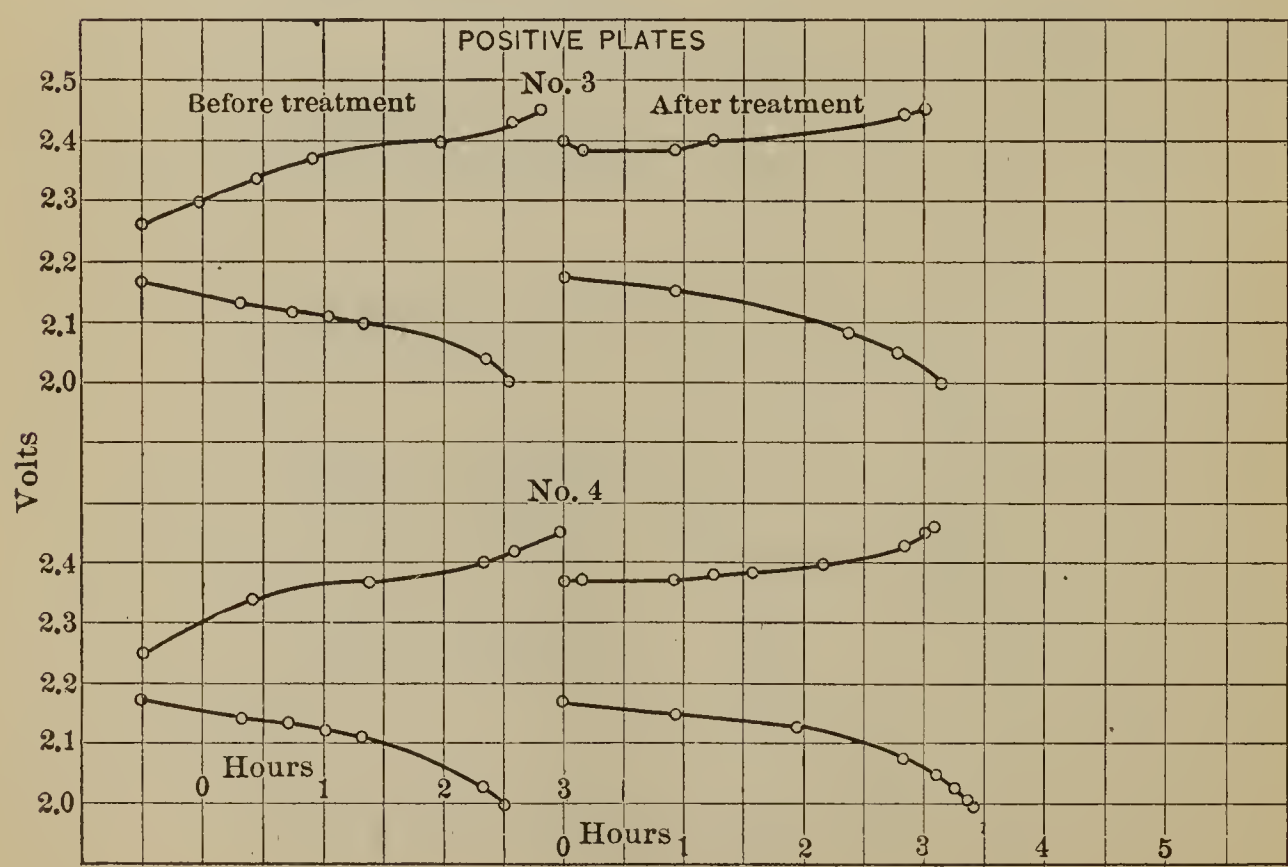
POSITIVE PLATES
No. 3
Before treatment
After treatment
2.5
2.4
2.3
2.2
2.1
2.0
Volts
No. 4
2.4
2.3
2.2
2.1
2.0
Hours
0
1
2
3
Hours
0
1
2
3
4
5

FIG. 8.

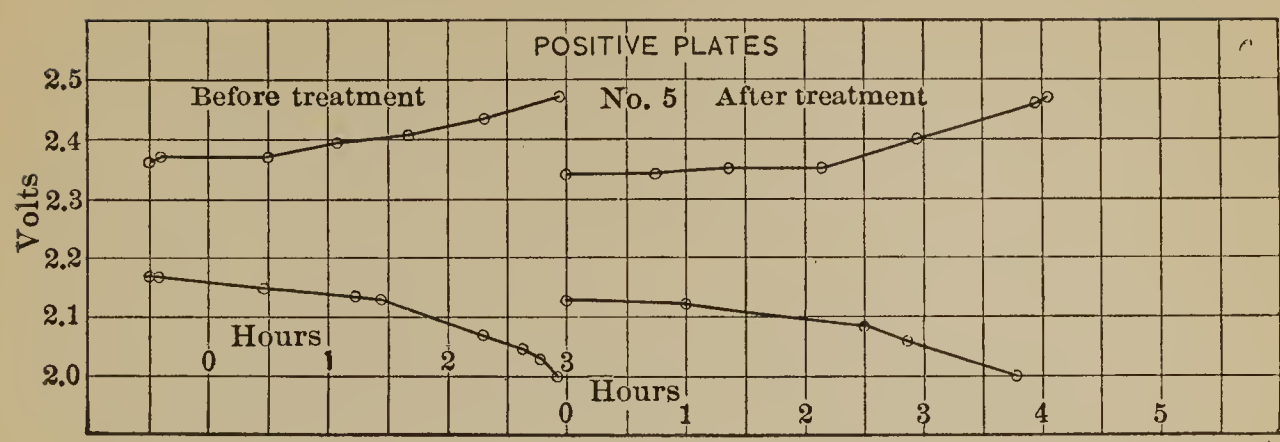

FIG. 9.

CONCLUSION.

The method of treatment used on negative plate No. 12 and positive No. 5 seems to give results superior to any of those tried; however, the method used on negatives 9 and 2 and positive 2 and 3 were close seconds. A formalin solution which was used in treating negatives 4 and 6 could not be applied to positive plates. The use of formalin is also objectionable, because the plates are very hard to free from this substance. The results show that acid drying is very harmful to negatives; however, it does not decrease the capacity or injure the physical condition of positive plates. It is therefore preferable to treat complete battery elements by the method applied to negative No. 12. However, when the application of this method is very inconvenient, as would be the case with large stationary batteries, the method applied to negative No. 11 and positive No. 1 should be used.

Electrochemical Laboratory,
Indiana University.

A paper read by title at the Twelfth General Meeting of the American Electrochemical Society, in New York City, October 19, 1907; President C. F. Burgess in the chair.

ON THE ELECTROLYTIC REDUCTION OF NITRIC ACID.*

By Harrison E. Patten.

Introduction.

Schönbein,[1] in 1839, stated that hydrogen reduces nitric acid at the cathode only when the acid is concentrated, and Brester[2] later showed that ammonia may also be formed from *dilute* nitric acid subjected to electrolysis. Thorpe[3] studied the electrolytic reduction of nitrates and nitrites in considerable detail. Tommasi[4] found that electrolysis of potassium nitrite gave only ammonia while ammonium nitrite and ammonia were formed by electrolyzing potassium nitrate. Zorn[5] electrolyzed concentrated sodium nitrite solution with four Bunsen elements, using platinum cathode, and obtained only ammonia, not the slightest trace of hydroxylamine or of nitrous acid; but with mercury as cathode he got both nitrite and hydroxylamine. Zorn recognizes that sodium amalgam[6] is probably formed first at the mercury cathode, and then acts upon the nitrate to reduce it. He states, too, that the same reduction products come from nitrate as from nitrite, but it takes longer to get them from the nitrate, since it must first be reduced to nitrite. The more extended investigations upon the electrolytic reduction of nitric acid have been controlled and influenced by different standpoints.

Thus, Luckow[7] found that addition of copper sulphate aids in the electrolytic reduction of nitric acid to ammonia; and

* Published by permission of the Secretary of Agriculture.

[1] Pogg. Ann., **47**, 563 (1839).

[2] Archives de Genéve, **28**, 60 (1867); also, Archives Neér., **1**, 296 (1866).

[3] Jour. Chem. Soc., **2**, 541 (1873).

[4] Elektrochimie, **7**, 633, 647.

[5] Ber., **12**, 1509 (1879).

[6] Compare E. Divers, Reduction of an alkali nitrite by an alkali metal. Jour. Chem. Soc., **43**, 443 (1883); also, Acworth and Armstrong, Ibid. [2], **2** (1877).

[7] Zeit. analyt. Chem., **19**, 11 (1880).

Vortmann,[8] in 1890, proposed to estimate nitrates by quantitative reduction to ammonia in sulphuric acid solution, using platinum electrodes plated with copper which deposited from copper sulphate added to the electrolyte. His determinations agree well with each other and with the theoretical yield of ammonia, but the very small current and long time required, and especially the need of reversing the current to maintain continuous deposition of the copper at the cathode are serious defects in the method. At this early date, the effect of current density or cathode potential upon the reduction was not recognized, but Vortmann realized clearly the effect of concentration, especially that of the nitrate and of copper sulphate. Most important is his discovery that the continuous deposition of copper, platinum, mercury, or zinc from solution aids in the completeness of the reduction. He advances no explanation for this effect of the depositing metal. Vortmann's maximum experimental error was 1 per cent. for the nitrogen in potassium nitrate, and 2.5 per cent. when copper nitrate was used. He gives a current equivalent to 1 to 2 c.c. electrolytic gas per minute, which is approximately .05 ampere, but the size of the electrodes is not stated, so the current density may be surmized only in a rough way from the fact that a platinum dish was used, which may have held from 50 to 200 c.c. No mention is made of the possibility of the formation of hydroxylamine or of the possibility of re-oxidation at the anode, the cell containing no diaphragm; reversal of the current gave a copper anode, so he thought that anode oxidation would be confined mostly to the copper. No statement is made as to the length of time required, nor is the temperature mentioned. Ulsch,[9] too, has shown that nitrates may be quantitatively converted to ammonia in acid solution at a copper cathode, while platinum, lead and mercury cathodes give different products of electrolysis in varying amounts. It should be borne in mind, however, that the most important detail of Ulsch's method consists in oxidizing the copper cathode by heating to redness and plunging into water; according to Ulsch, this coating of copper oxide, whatever may be the true nature of its function, is necessary for

[8] Ber., 23, 2798 (1890).

[9] Zeit. Elektrochem., 3, 546 (1896).

the quantitative conversion of nitrates to ammonia. A bright copper cathode loses its reducing power during an experiment. The effectiveness of this copper oxide coating, together with the nitrate in solution, in fixing hydrogen at the cathode, is shown by the fact that 90 per cent. of the nitrate (using .202 gram potassium nitrate [KNO_3] in 20 c.c. solution, .5 normal with respect to sulphuric acid [H_2SO_4], and a current density of 1.47 amperes per sq. dm.) was converted to ammonia before any gas was evolved at the cathode, which was copper wire 2 m. long, 1 m. in diameter, and coiled spirally. The anode here was a thin platinum wire 20 cm. long.

Thus the methods of Vortmann and of Ulsch are really similar, differing only in the substance and reaction used to prevent liberation of hydrogen by the current in excess of that used for the reduction of the nitrate. A similar procedure, using oxidized cathodes of lead, mercury, zinc, etc., is needed before we can compare Ulsch's results for an oxidized copper cathode with other metals.

Zechlin[10] showed that the yield of ammonia and of hydroxylamine is greatly dependent upon the cathode material, but he obtained hydroxylamine at all the cathodes used—zinc, copper, nickel gauze, platinum, and amalgamated zinc, copper and mercury; while nitrite is formed only at a mercury cathode or at an amalgamated cathode of copper or zinc. Using nickel, he got 60.9 to 76.8 per cent. current yield of ammonia. With a zinc cathode under the same conditions, the yield was 64.6 to 71.8 per cent. hydroxylamine, with only 23.4 per cent. of ammonia.

Ihle[11] determined the limiting current density at which ammonia is formed at a platinum cathode in several concentrations of nitric acid. The cathode products were not determined quantitatively. He measured the polarization of the total cell at each of these current densities, but did not take single potential discharges from the cathode, although in a paper[12] following immediately in the same journal he measured the single potential of platinum in nitric acid of varying concentration, as well as

[10] Inaug. Dis. Giessen (1899).

[11] Zeit. phys. Chem., **19**, 574 (1896).

[12] Ibid., **19**, 584 (1896).

the effect upon this single potential produced by adding urea and potassium nitrite.

Tafel[13] so modified the reduction of nitric acid at amalgamated lead cathodes that 90 per cent. of hydroxylamine, and only 5 per cent. of ammonia, was obtained. Using lead, amalgamated lead, tin, silver and copper cathodes with a closed porous-cup cathode chamber, he determined the nitrogen and nitrous acid loss at the cathode, as well as the hydroxylamine and ammonia formed. Tafel's highest yield of ammonia at a spongy copper cathode is 93.8 per cent., with 1.5 per cent. hydroxylamine and .1 per cent. of nitrous acid, the duplicate being slightly lower—92.3 per cent. of the theoretical, with 1 per cent. of hydroxylamine. This last experiment showed a small volume of nitrogen given off at the cathode. The current density used was 24 amperes per sq. dm. Tafel electrolyzed hydroxylamine at a copper cathode without being able to observe the slightest reduction, and therefore concludes that the electrolytic reduction of nitric acid to ammonia at copper electrodes does not go through hydroxylamine as an intermediate stage.

In all of the foregoing work, the specific influence of the cathode metal upon the products of reduction is clear. The completeness of the reduction appears not to parallel the position of the cathode metal in the electrochemical series, and the overvoltage produced by a hydrogen polarization at the cathode—Caspari's effect[14]—likewise fails to explain why copper gives the highest yield of ammonia, and platinum, lead and mercury much lower yields. The experimentation thus cited was carried out with definite current density, concentration and temperature, but very little attention was paid to the cathode polarization during the course of the reaction.

A number of authors[15] have recognized and made exact practical application of the principle of graded electrode potential since Tafel's work appeared. For example, Löb and Moore,[16] by the reduction of nitrobenzene in 2 per cent. sodium hydroxide solution, obtained the same product in similar yield by main-

[13] Zeit. anorg. Chem., **31**, 289 (1902).

[14] Zeit. phys. Chem., **30**, 89 (1899).

[15] Nernst, Ber. deutsch. chem. Ges., **30**, 1561 (1897); Haber, Zeit. Elektrochem., **4**, 506 (1898); Zeit. phys. Chem., **32**, 256 (1900); Dony-Henault, Ibid., **6**, 539 (1900); Coehn and Billitzer, Ibid., **7**, 682 (1901); Löb, Zeit. Elektrochem., **7**, 320, 333 (1900).

[16] Zeit. phys. Chem., **47**, 418 (1904).

taining the cathode potential at a constant value, regardless of the electrode or the substance added in solution. And Tafel[17] and his assistants have shown that the reduction of difficultly reducible organic substances is possible only by using a cathode material which shows a high cathode polarization. One expects similar considerations to hold in the reduction of inorganic bodies.

Flaschner[18] has recently investigated the reduction of hydroxylamine and of nitrous acid at different cathodes, keeping the cathode potential approximately constant. This steady cathode polarization was effected by increasing or decreasing the current density. The choice of cathode potential was made by first determining the cathode decomposition voltage for the solution and cathode material desired, and then carrying out the reduction at a cathode polarization slightly below this value; all evolution of hydrogen was thus avoided. Flaschner found that the rule of graded potential is of limited application. The cases in which its simple use does not lead to the practical separation of the reduction products may be stated thus: (1) A gradation is possible only when the decrease in oxygen content of the reduced substance likewise corresponds to a decrease in the oxidation potential. Haber has found a reduction product which possesses a higher oxidation potential than the original substance from which it was formed. Thus, no necessary correspondence between oxygen content and oxidation potential exists. (2) The electrode metal exercises such an influence upon the speed of the reduction that the effect of other factors is masked. (3) It is not found that each reduction must pass through all the intermediate stages. The formation of these intermediate substances is only to be assumed as probable, from kinetic considerations. (4) The reduction experiments confirmed the results expected from a consideration of the preliminary decomposition point measurements. (5) The rule of graded potential is not applicable in a simple way to the reduction of hydroxylamine, since even at low cathode potential the end product of the reduction is formed. (6) The speed of reduction of hydroxylamine and of nitrous acid is different at

[17] Zeit. phys. Chem., **34**, 187 (1900); **50**, 715 (1905); **54**, 433 (1906).

[18] Monatshefte Chem., **28**, 209 (1907).

cathodes of different metals. Platinized platinum gives to the reduction a relatively great velocity, which is to be attributed to the catalytic effect of the platinum sponge. (7) At copper cathodes, nitrous acid, as well as nitric acid, is reduced only to ammonia. (8) In the reduction at a potential below the hydrogen-evolution potential, where no gas is liberated, there was always a large waste of current. (9) The temperature effect is slight in the reduction of nitrous acid.

In the present paper, a series of measurements is presented in which no attempt was made to maintain the cathode potential constant.

STATEMENT OF THE PROBLEM.

The factors which are involved in all electrolytic processes have to be dealt with here, namely, influences of electrode voltage, electrode material, current density, temperature, composition, and concentration of electrolyte. Disturbing influences, such as secondary products formed at the electrode cells and decomposition of the main products of electrolysis at the anode, must also be taken into account. The experimental results will be grouped mainly from the standpoint of the yield of ammonia. *First,* in order to get a view of the initial electrode potential in the solution, single potential measurements were made, using different metals. These, together with the decomposition voltage measurements of Flaschner,[19] give an insight into the reactions which may be expected under actual conditions of electrolysis. *Second,* a series of experiments using a copper cathode with a porous-cup diaphragm and a lead anode in dilute sulphuric acid was run, in which the effect of the concentration of the sulphuric acid was found first upon the yield of ammonia, and second, upon the yield of hydroxylamine; at the same time, discharge potentials were taken for the cathode during the process of electrolysis. *Third,* the effect of current density upon the yield of ammonia and hydroxylamine was determined, using a porous-cup diaphragm with a copper cathode, and with a lead cathode. Here also discharge potentials were taken. *Fourth,* the effect of temperature upon yield was studied. *Fifth,* the effect of dissolved copper sulphate upon the yield of

[19] l. c.

ammonia at a copper cathode and at an amalgamated copper cathode was found; and for comparison, experiments were made with no copper sulphate present, using, on the one hand, a pure copper cathode, and on the other, a pure mercury cathode. Then a number of experiments were carried out under conditions which have been recommended in the literature for the quantitative conversion of nitrate to ammonia. In some of these runs, very complete anode and cathode discharge potential measurements were taken during the course of the reduction, and the yield of ammonia and of hydroxylamine determined. *Sixth,* the influence of the cathode material upon the yield of ammonia and of hydroxylamine was studied, using zinc, lead, aluminum, platinum, copper, copper-plated platinum, amalgamated copper, and mercury. For the sake of comparison, a few reductions of nitrate in alkaline solution were made, using platinum, copper and zinc cathodes with a platinum anode. The discharge potentials and the yields of ammonia were found. *Seventh,* as an outcome of the experiments in the fifth and sixth sections, it seemed likely that a loss of nitrogen occurred at the anode. To investigate this, the anode and cathode gases, for a series of reductions, were collected and analyzed, and the yields of ammonia and hydroxylamine likewise determined. *Eighth,* the persistent occurrence of hydroxylamine in the electrolyzed solutions suggested the question as to the reducibility of hydroxylamine at a copper cathode. Consequently, a series of experiments was run, starting with hydroxylamine hydrochloride, and the yield of ammonia, the residual hydroxylamine, and the anode and cathode discharge potentials taken, using a copper cathode with a platinum anode in a glass beaker. The effect of copper sulphate in solution upon this reduction of hydroxylamine was likewise shown, maintaining the foregoing conditions the same in other respects. *Ninth,* similarly, it was deemed advisable to study the reduction of nitrite, using a copper cathode and platinum anode. Here also discharge potentials at anode and cathode were taken. The yield of ammonia and of reducible material remaining was estimated, and the influence of copper sulphate in solution upon the reduction of nitrite determined.

EXPERIMENTAL METHODS.

Electrolytic procedure:

The electrolytic reductions were carried out in five different cells: (1) A glass beaker of some 500 c.c. capacity, which served as the anode chamber, in which was placed an anode of small lead pipe, wound around a porous cup of 150 c.c. capacity, that held the cathode solution. The anode solution was dilute sulphuric acid. This cell is shown in Fig. 1. (2) A simple glass beaker containing a small platinum anode, with the large cathode of sheet metal bent in cylindrical form, as shown in Fig. 2. (3) A wide-mouth flask, holding 300 c.c., closed by a rubber cork, through which passed wires leading to the small

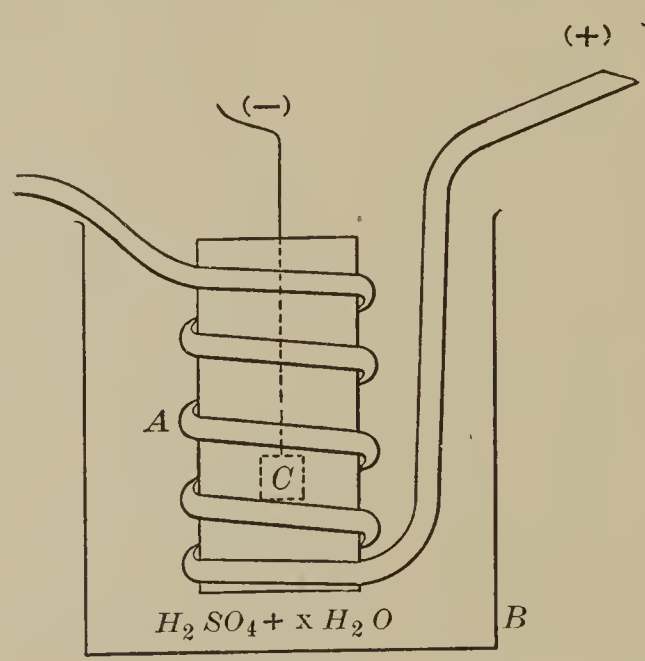

FIGURE 1

anode of platinum and the large cathode of sheet metal, as shown in Fig. 3. This cell was used for the reduction of nitrates in alkaline solution. The exit tube, labeled G, served to conduct the gases evolved through an absorption tube containing standard sulphuric acid, which served to retain any ammonia or gaseous products of a basic nature escaping from the alkaline solution. The experimental data show that such an absorption tube was not necessary. The siphon tube H is filled with caustic potash solution and closed at its lower end, within the electrolytic cell, by a plug of asbestos fiber, which serves to prevent diffusion. Its other end dips into an intermediate cell containing potassium chloride solution, which serves to connect the electrolytic cell

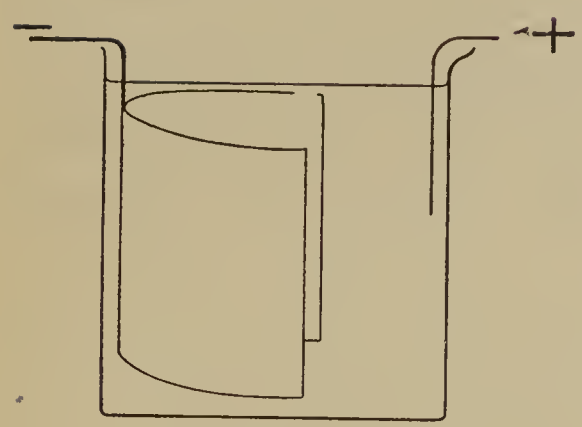

FIG. 2.

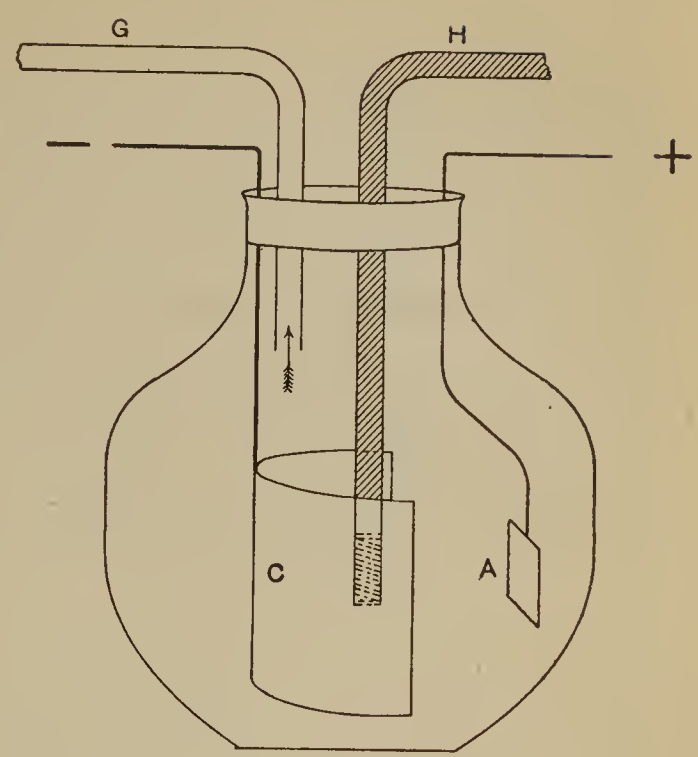

FIG. 3.

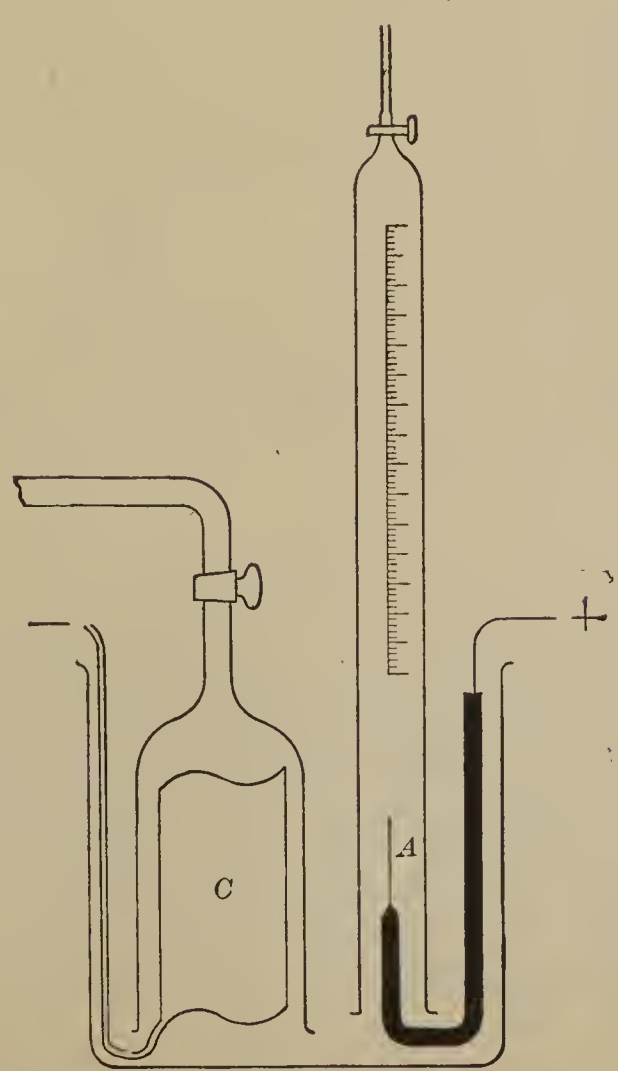

FIG. 4.

with the N/10 calomel electrode used in taking discharge potentials at anode and cathode from time to time during the electrolysis. (4) Where the gases evolved at anode and cathode were collected and analyzed, the form of cell shown in Fig. 4 was used. The chamber for the anode gases was an ordinary 50 c.c. burette, graduated in tenths, inverted over the platinum anode, which consisted of a fine wire fused into a bent glass tube, electrical connection being established by means of mercury within the glass tube. Owing to the large size of the cathode required, a similar graduated glass chamber was not used.

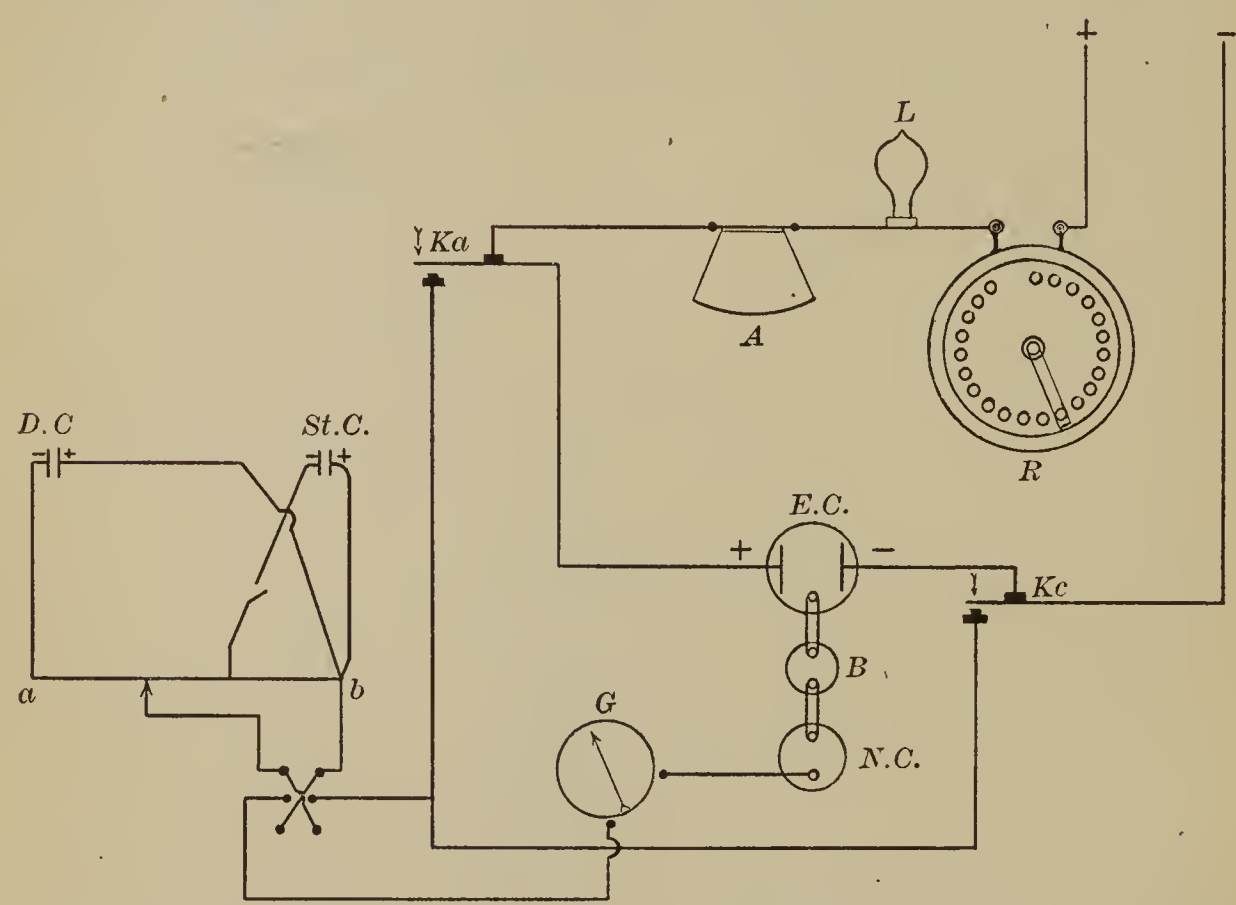

FIG. 5.

Instead, a cylindrical straight-walled separatory funnel, 3.5 cm. in diameter and 10 cm. high, was inverted over the cathode. The exit tube from this was connected with a gas pipette, which permitted removal of the cathode gas at will, and also the stirring of the cathode solution, from time to time, by drawing the gas back and forth between the cathode chamber and the gas pipette. This prevented the exhaustion of the solution present in the cathode chamber before the rest of the solution in the beaker had been acted upon. (5) A water-cooled test tube containing a copper spiral as cathode, with a platinum wire in the axis of the spiral serving as anode, as shown in Fig. 6.

Electrical measurements:

The current was measured by a Weston ammeter reading to hundredths of an ampere. The discharge voltage, single potential, was determined by means of an Ostwald half-cell; the voltage, electrode-solution-half-cell, being measured by the compensation method on a slide-wire bridge against a Leclanché dry cell, whose value was taken from time to time by comparison with a Weston standard cell, whose value was

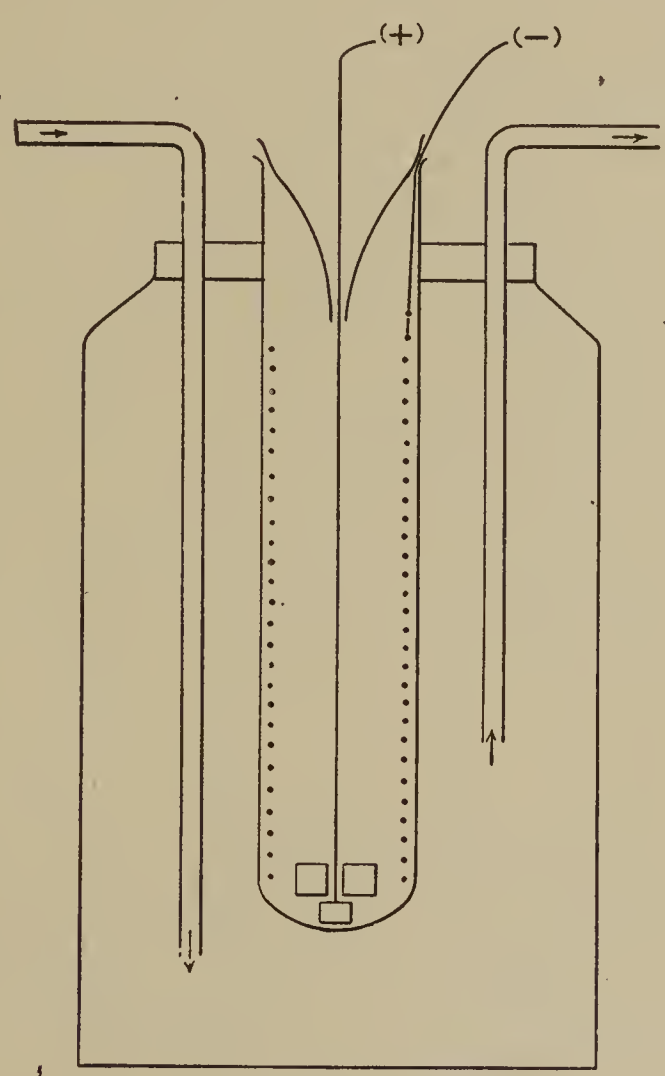

FIGURE 6

1.0193 volts.[20] This discharge potential was taken by interrupting the current momentarily during the process of electrolysis. The electrical connections used are shown in conventional form in Fig. 5. Starting with the positive terminal of the dynamo, R is an adjustable resistance, and L an incandescent lamp in series with the ammeter A. The current passes thence to the electrolytic cell, EC, and from there back to the

[20] This cell was numbered 825, Bureau of Standards collection, and was kindly loaned to us for this research.

negative terminal of the dynamo. The half-cell, NC, is connected by a glass siphon tube with the intermediate beaker B, from which a siphon plugged with asbestos leads into the electrolytic cell. When the current in the main circuit is interrupted by closing the spring key K, in the direction indicated by the arrow, a current passes from the electrolytic cell through B, through NC, through the galvanometer G, to the double-point switch, and thence to the slide-wire bridge ab, from which it returns through b back to the double-point switch, on through the key Ka, to the positive electrode of the electrolytic cell. In order to obtain a discharge potential from the cathode, one presses the key Kc in the direction indicated by the arrow, when the current passes, as before, from EC to B, to NC, to G, to the switch, to the wire ab, and then back through b to the switch, and through the negative electrode. The direction in which the current flows when the key Kc is pressed will depend upon whether the discharge potential at the cathode is greater than the value of the normal cell, NC, or not. This is likewise true for the direction of the current flow during the anode discharge.

Regarding the constancy of the dry Leclanché cell, it should be said that its variation consists in a regular drop in voltage which is not hard to follow within the limits of experimental error of the present research by frequent comparison with a standard Weston cell. The galvanometer G was a d'Arsonval of the portable type, having a resistance of 847 ohms. One volt through one megohm gave a deflection of one scale division. Its delicacy was all that could be desired in the present investigation. The value of the .1 N calomel electrode, as given by Palmaer,[21] is used here,—.5732 volt at 18° C.

Analytical methods:

The nitrate solutions in general were made of 10 grams of potassium nitrate per liter, and measured out by a pipette as desired. Similarly, a copper sulphate solution containing 10 grams per liter was used, but in a number of the experiments the copper sulphate ($CuSO_4.5H_2O$) was weighed out directly. The nitrogen content of the potassium nitrate was determined by an indirect method. The solution was analyzed, the potassium

[21] Zeit. phys. Chem., 59, 129 (1907).

being weighed as potassium sulphate, and found to correspond to the theoretical quantity of KNO_3. The solution also gave no indication of nitrite. The solution remaining after electrolysis was analyzed for hydroxylamine by the addition of a N/10 potassium permanganate solution, which was also standardized against a known solution of hydroxylamine. While the end point of this titration, omitting the ferrous sulphate as ordinarily recommended, is not so sharp as might be desired, it is still sufficiently pronounced to give a good control of the electrolytic reduction, especially when taken in connection with the yield of ammonia from this same solution, which was most accurately determined. The ammonia remaining in the electrolyzed solution after the hydroxylamine had been destroyed with permanganate was estimated by rendering alkaline with potassium hydroxide in considerable excess and distilling over into standardized sulphuric acid. Duplicate analyses thus determined checked in the most satisfactory manner. Where it was desired to determine nitrite, the method of Nef and Kinnicut[22] was used, a few drops of permanganate being added first, then dilute sulphuric acid, then permanganate to excess, and finally, the residual permanganate determined with standard oxalic acid.

Determination of gases:

Where the anode gases were collected and examined, a fraction of some 50 c.c., accurately measured, was absorbed by alkaline pyrogallol repeatedly until no further contraction took place, and the residual gas taken as nitrogen. In a few cases, this anode gas was absorbed by phosphorus, but the high percentage of oxygen renders this procedure inadvisable, owing to the great heat developed. Consequently, the use of phosphorus was discontinued.

The gas evolved at the cathode was absorbed by regenerated palladium sponge, and the residual gas taken as nitrogen. In every case, this residual gas was subjected to repeated treatment with freshly regenerated palladium sponge. It should be stated that the palladium absorption tube used had a capacity for hydrogen of 66 to 68 c.c. at about 30° C. and 760 mm., conse-

[22] Sutton, Volumetric Analysis, p. 273, ninth edition (1904); see also Ber Suler, Zeit. Elektrochem. 7, 831 (1900-1901).

quently, in a residual volume of .3 to .8 c.c., which has been repeatedly passed over a palladium sponge, one may safely say that the hydrogen is all removed. And in this particular investigation, with the substances known to be present, it seems fairly evident that the bulk of this residual gas actually is nitrogen. Within the scope of this investigation, it was not possible to enter in more detail into the composition of these gases at anode and cathode. The rate at which these residual gases are evolved, and their bearing in a quantitative manner upon the electrolytic processes under the circumstances, served very well the needs of the investigation at its present stage.

Section I.

Preliminary Measurements of the Single Potential and Hydrogen-evolution Potential of Various Metals.

Table I gives the single potential of several metals in nitrate, nitrite, and acid solutions. The concentration of potassium nitrate and of sulphuric acid (given in a footnote to the table) for column 2 was chosen because it had been recommended in the literature as suitable for the quantitative reduction of nitrate to ammonia. The solution used for the values in column 3 is the same as in column 2, with the sulphuric acid omitted, while column 9 shows the single potentials in sulphuric acid when no potassium nitrate is present. The values in columns 4, 5 and 6 show the effects of concentration upon the single potential of each metal in nitric acid alone, while the values in column 8 for potassium nitrate solution serve to compare the depolarizing action of nitrate and nitrite.

Considering first the single potential of copper, we see that none of these values are so low as Neumann's,[23] —0.615 volt for KNO_3. Mott's value, —0.47 volt for 0.1 normal H_2SO_4, is very near to ours for 0.35 normal acid, —0.476 volt. His value for KNO_2, —0.44 volt, is higher than for sulphuric acid, but the single potential in nitric acid, —0.5 volt, is lower, as would be expected. It is hardly fair to consider the single potential of a neutral nitrate or nitrite as a test of its depolarizing power in acid solution. Thus we found, in another experiment, that a 0.1 normal $NaNO_2$ solution, when neutral, gave for copper —0.36 volt,

[23] l. c.

TABLE I.

Single potentials of metals in nitrate, nitrite, and acid solutions, at 25° C.

(1) Metal.	(2) KNO_3+ H_2SO_4	(3) 0.1 N KNO_3	(4) 0.1 N HNO_3	(5) N HNO_3	(6) Fuming Nitric Acid.	(7) 0.1 N H_2SO_4	(8) 0.1 N KNO_2	(9) 1.71 Per Cent. H_2SO_4
	Volts.	Volts.	Volts.	Volts.	Volts.	Volts.	Volts.	Volts.
Mg	+1.227	.....	+0.94	+0.79	.....	+1.27	+0.76	+1.239
Al	−0.032	.....	−0.03	+0.16	+0.70	+0.04	+0.73	.....
	−0.093	+0.775†	−0.01	−0.12	−0.76	−0.02	+0.40	.....
Zn	+0.513	+0.409*	+0.48	+0.40	+0.42	+0.45	.....	+0.520*
Cd	+0.231	+0.122†	+0.12	+0.10	+0.10	+0.22	.....	+0.231
Pb	+0.058	−0.115†	−0.058	−0.06	−0.35	−0.23	.....	.....
Ni	−0.284	−0.060†	−0.47	−0.49	−0.58	−0.38	+0.03	−0.022
Bi	−0.418	.....	−0.48	−0.50	.....	−0.44	−0.25	−0.385
Cu (Amalg.)	−0.431	.....	.....	.....	.....	.....	.....	−0.476
Cu	−0.436	−0.615†	−0.50	−0.51	−0.48	−0.47	−0.44	−0.476
Ag	−0.521	.....	.....	.....	.....	.....	.....	−0.974†
Sn	−0.652	.....	.....	.....	.....	.....	.....	.....
Hg	−0.786	−0.739	.....	.....	.....	.....	.....	−0.980
Pt (Polished)	−0.910	−0.658	−1.11	−1.22	−1.34	−0.96	−0.80	−0.777

(2) Solution: 1.000 gram KNO_3 and 1.715 gram H_2SO_4 per 100 c.c.

(3) Solution: 1.00 gram KNO_3 per 100 c.c. (except for values by other experimenters); practically 0.1 normal.

The data in columns 4, 5, 6, 7 and 8 are taken from unpublished determinations made by Mr. W. R. Mott.

(9) This H_2SO_4 is 0.35 normal.

* From unpublished data by Patten and Mott. † Neumann, Zeit. phys. Chem., **14**, 229 (1894).

single potential; and when acidified with H_2SO_4, —0.522 volt. Further, the single potential, —0.436 volt of copper in acidified nitrate solution, given in column 2, is not so low as the discharge potential obtained at a copper cathode during electrolysis of this same solution, which at times was as low as —0.5 volt. This difference is probably due to a hydrogen polarization, where the metal is simply immersed in the liquid, and no especial stirring occurs.

These single potential measurements show that both nitric acid and nitrous acid depolarize a copper cathode, all the values being much below the hydrogen polarization on copper. The single potential of copper in hydroxylamine hydrochloride solution, 0.42 normal, was —0.509 volt; and when sulphuric acid was added, the potential rose to —0.441 volt, showing that this body likewise acts as a depolarizer at a copper cathode, and should be reduced when electrolyzed.

Similar relations are shown by the other metals—lead, nickel, cadmium, zinc and magnesium. Aluminum, as might be expected, shows variations, owing to the formation of a thin film[24] upon its surface in presence of oxidizing material. Bismuth, silver and mercury, on the other hand, show a slight rise in single potential when nitrates are added to the sulphuric acid solution.

It is to be borne in mind, however, that the hydrogen polarization potential is the value to which reference should be made when considering the depolarizing action of a nitrate or other reducible body, and these values, given in Table I, are single potential measurements taken at the moment when the metal is dipped into the solution. The hydrogen potential at the metals would be higher than the single potential, and, too, the voltage at which hydrogen is liberated upon a metal is a function of the current density.

Nutton and Law[25] have recently determined the hydrogen polarization potential for several metals in various solutions.

[24] Kahlenberg, Electrochem. Ind., **1**, 1, 201 (1903); Isenburg, Zeit. Elektrochem., **9**, 278 (1903); Cook, Physical Review, **18**, 23 (1904); F. Fischer, Zeit. phys. Chem., **48**, 177 (1904); F. Krüger, Ibid., **45**, 1 (1903); Burgess and Hambuechen, Trans. Am. Elect. Chem. Soc., **1**, 147 (1902); Electrochem. Ind., **1**, 6, 204 (1903); Mott, Electrochem. Industry, **2**, 4, 7, 129, 268 (1904); C. I. Zimmerman, Trans. Am. Electrochem. Soc., **5**, 147 (1904); Patten, Jour. Phys. Chem., **7**, 153 (1903); **8**, 548 (1904); Schulze, Ann. d. Physik [4], **24**, 43 (1907).

[25] Trans. Faraday Soc., **3**, 51 (1907).

Table II.

The single potential of hydrogen liberated at various cathodes in acid and in alkaline solution, according to Nutton and Law.

Current Density Per Sq. Cm.	Copper.		Platinum.		Nickel I in 5% KOH.	Nickel II in 5% KOH.	Tin I in 5% H_2SO_4.	Tin II in 5% H_2SO_4.	Tin in 5% KOH.	Magnesium in 5% KOH.	Iron in 5% KOH.	Aluminum in 5% H_2SO_4.	Zinc in 5% KOH.	Zinc (Amalg.)* in 5% KOH. 50% C_2H_5OH.	Zinc (Amalg.) in 5% H_2SO_4. 50% C_2H_5OH.	Cadmium in 5% KOH.	Cadmium in 5% H_2SO_4.	Lead in 5% H_2SO_4.	Lead (Amalg.) in 5% KOH. 50% C_2H_5OH.	Lead (Amalg.) in 5% H_2SO_4. 50% C_2H_5OH.	Current Density Per Sq. Cm.
	In 5% H_2SO_4.	In 5% KOH. 50% C_2H_5OH.	Platinized in 5% H_2SO_4.	Polished in 5% KOH.																	
Amp.	Volts.	Volts.	Volts.	Volts.	Volts.	Volts.	Volts.	Volts.	Volts.	Volts.	Volts.	Volts.	Volts.	Volts.	Volts.	Volts.	Volts.	Volts.	Volts.	Volts.	Amp.
0.0003	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	0.7016	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	0.0003
0.0005	0.334	0.4272	0.0103	0.2031	0.3723	0.2499	0.6249	0.6407	0.6084	0.7340	0.1480	0.4942	. . . .	0.9365	0.8626	0.5227	0.4320	0.5701	0.7127	0.7070	0.0005
0.0007	0.3509	0.4343	. . . .	0.2303	0.3957	0.2664	0.6459	0.6627	. . . .	. . . .	. . . .	0.5125	0.7548	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	0.0007
0.0008	0.3618	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	0.0008
0.0009	. . . .	0.5421	. . . .	0.2508	0.4131	0.2795	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	0.6028	. . . .	. . . .	0.0009
0.001	0.3663	0.4575	0.0148	0.2624	0.4191	0.2852	0.6587	0.6857	0.6515	0.7930	0.1741	0.5283	. . . .	0.9621	0.9536	0.5569	0.4723	0.6078	0.8055	0.7485	0.001
0.0015	0.3827	0.4743	. . . .	0.3078	. . . .	. . . .	. . . .	. . . .	. . . .	0.8170	0.1925	0.5464	. . . .	. . . .	. . . .	0.5744	. . . .	0.6297	. . . .	. . . .	0.0015
0.002	. . . .	. . . .	. . . .	. . . .	0.4699	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	0.8649	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	0.002
0.003	0.4083	0.5000	0.0232	. . .	. . .	0.3368	0.7026	0.7416	. . . .	0.8471	0.2232	. . . .	0.9142	0.9851	0.9748	0.6232	0.5149	0.6633	0.9101	0.7997	0.003
0.005	0.4245	0.5146	0.0273	0.3993	0.4924	0.3595	0.7220	0.7694	0.7775	0.8655	0.2496	0.5894	. . . .	0.9973	1.0045	0.7252	0.5325	0.6873	0.9544	0.8210	0.005
0.007	. . . .	. . . .	. . . .	. . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	0.9818	. . . .	. . . .	. . . .	. . . .	. . .	. . .	. . . .	0.007
0.0075	. . . .	0.5273	. . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. .	. . .	0.0075
0.01	0.4530	. . . .	0.0349	0.4567	0.5203	0.3871	0.7784	0.8071	0.8289	0.8868	. . . .	. . . .	. . . .	. . . .	. . . .	0.7702	0.5539	0.7038	1.0012	0.8756	0.01
0.015	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	0.6155	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	0.015
0.017	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	1.0800	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	0.017
0.025	. . . .	. . . .	. . . .	0.5352	0.5577	0.4288	0.8367	0.8892	0.9025	0.8950	0.3795	0.6537	. . . .	1.1632	1.2194	0.8244	0.5895	. . . .	1.0270	0.9420	0.025
0.033	. . . .	. . . .	. . . .	. . .	. . .	. . .	. . .	. . . .	. . .	. . . .	. . .	. . . .	1.1620	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	0.033
0.05	0.5287	0.5934	0.0890	0.6038	0.5870	0.4703	0.9000	0.9882	0.9575	0.9318	0.4470	0.6917	. . . .	1.2495	1.3799	0.8845	0.6304	0.7427	1.0687	1.0327	0.05

Note.—Where two sets of values are given for one metal, the difference is due to the physical condition of the metal.

* Mercury gave practically the same values as amalgamated zinc in potassium hydroxide, alcohol, water solution.

The variation in these values, assembled for convenient reference in Table II, is attributed mainly to the formation of a film upon the cathode surface. The effect of an impurity on a metallic surface depends upon the relative overvoltage of the coupled metals, and is governed by the metal at lowest overvoltage. The subsequent values of the determined e. m. f. depend upon the quantity of added metal, and the ease with which this diffuses into the original metallic surface.[26] The overvoltage is also influenced very considerably by the physical condition of the metallic surface of the cathode.

E. Müller[27] has measured the depolarization potential of normal solutions of potassium nitrate, hydroxylamine hydrochloride, and sodium nitrate, each solution being also 0.1 normal with reference to its content of potassium hydroxide. At platinized platinum, the current-voltage curves for potassium nitrate and potassium sulphate coincide; this means that the the depolarization potential of potassium nitrate is no lower than the hydrogen polarization. The portion of the current used in reducing potassium nitrate was only 14.8 per cent., the remainder of the current being used for hydrogen evolution. For normal sodium nitrite solution at platinized platinum, the depolarization potential is about 0.4 volt lower than for potassium sulphate, consequently we may expect a higher proportion of the current to be used in reduction. And this was found to be true, 29.4 per cent. of the current going to reduce the nitrate under favorable conditions. For hydroxylamine hydrochloride, a strong current passed through the cell at —0.41 volt cathode potential, whereas the hydrogen evolution potential is +0.42 volt in the comparison solution; the depolarization therefore amounts to some 0.8 volt. Thus, the oxidizing power of hydroxylamine in alkaline solution appears to be greater than either nitrate or nitrite. Müller observes that this is paralleled by the fact that he has never been able to establish the presence of hydroxylamine in large amount in the electrolysis of neutral solutions of nitrate and nitrite. The positive proof that the total current is used for reduction in the case of hydroxylamine has not been given by Müller.

[26] See Law and Chapman. The effect of impurities upon the reducing power of zinc in acid solution. Analyst, , 5 (1906).

[27] Zeit. anorg. Chem., **26**, 1 (1900).

TABLE III.

Depolarization of various metallic cathodes by nitric acid and by hydroxylamine, as shown by current-voltage curves, according to Flaschner.*

Platinized Platinum Point.								Copper.							
1 N. H_2SO_4		8 N. HNO_3		1 N. HNO_3		⅛ N. HNO_3		N. H_2SO_4		8 N. HNO_3		1 N. HNO_3		⅛ N. HNO_3	
v (†)	i (‡)	v	i	v	i	v	i	v	i	v	i	v	i	v	i
—0.826	50 8	—0.634	51.1	—0.828	50.3	—0.580	50.8	—0.241	49.9	—0.250	53.5	—0.213	50.2	—0.218	50 3
—0.630	50.7	—0 472	51.7	—0 632	50 9	—0.390	50.6	—0.050	50.6	—0.240	79	—0.118	51	—0 120	50.5
—0.429	50.6	—0.384	53.2	—0.439	51.8	—0.198	53.2	+0.132	50.9	. . . . .	. . . . .	—0.040	57	—0.022	50.8
—0.237	50.8	—0.285	61	—0 257	59	—0.108	54	+0.311	55.7	. . . .	. . . . .	+0.006	∞	+0.034	54.6
—0.044	51.9	—0.236	75	—0.190	84.6	—0.010	56	+0.347	75	. . . . .	. . . . .	. . . .	. . . .	+0.074	69.5
+0 034	∞	. . . .	. . . .	. . . .	. . . .	+0 044	63	+0 405	∞	. . . . .	. . . . .	. . . .	. . . .	. . . . .	. . . . .

Mercury.						Polished Platinum.				Plat'd Plat'm Pt.		Copper.			
1 N. H_2SO_4		$(NH_2OH)_2$ H_2SO_4		2 N. HNO_3		1 N. H_2SO_4		1 N. $(NH_2OH)_2H_2SO_4$		1 N. (?) $(NH_2OH)_2H_2SO_4$		1 N. H_2SO_4		1 N. $(NH_2OH)_2H_2SO_4$	
v	i	v	i	v	i	v	i	v	i	v	i	v	i	v	i
+0.194	50.1	+0.53	50.2	+0.163	50.1	—0.213	50 2	0	50.1	—0.304	51.3	—0.050	50.6	—0.210	50.2
+0.387	50.2	+0.758	50 4	+0.365	50 3	+0.024	50.2	+0.092	50.8	—0.214	55.6	+0.132	50.9	—0.014	50.6
+0.591	50.2	+0 972	52.6	+0.558	50.4	+0.126	50.7	+0.152	51.6	—0.132	67.5	+0.311	55.7	+0.170	53.8
+0.794	50.5	+1.069	61	+0.748	50.7	+0.240	54 9	+0.189	53.2	—0.08	65.5	+0.347	75	+0.256	68.2
+0.984	53.3	+1.134	∞	+0.839	52.6	+0.315	68.3	+0.226	55.6	—0.06	65	+0.405	∞	+0.29	79.6
+1 075	58.6	. . . .	. . . .	+0.925	63.7	. . . .	. . . .	+0.259	60.3	—0.02	58	. . . .	. . . .	. . . . .	. . . . .
+1.145	77	. . . .	. . . .	+0.982	. . . .	. . . .	. . . .	+0.296	68.8	+0.024	58.6	. . . .	. . . .	. . . .	. . . . .
. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	+0.320	79.5	+0.032	72.7	. . . .	. . . .	. . . . .	. . . . .
. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . . .	. . . . .	+0.038	∞	. . . .	. . . .	. . . . .	. . . . .

* Monatshefte für Chem., **28**, 216-220 (1907).

† v = cathode polarization in volts.

‡ i = galvanometer deflection, zero = 50 on the galvanometer scale.

Flaschner's[28] decomposition point curves, given in Table III, show the depolarizing effect of nitric acid and hydroxylamine at mercury, copper and platinum. The current voltage curves for hydroxylamine very nearly coincide with that for pure sulphuric acid, while the twice normal nitric acid shows a considerable lowering of the decomposition voltage. From this, it would be concluded that the depolarization potential of the hydroxylamine lies as high, if not higher, than the polarization obtainable in sulphuric acid—that is, that hydroxylamine is hardly at all reduced at a mercury cathode, *i. e.,* the reduction of nitric acid remains at the hydroxylamine stage.[29] At polished platinum, hydroxylamine shows a slight depolarization, while at a copper cathode the depolarization is much greater, amounting to 0.1 volt.

Flaschner points out, too, that the maintenance of cathodes of different metals, with their corresponding overvoltage, at the *same potential* by *different current* densities, has its origin in the catalytic acceleration of the reduction by the cathode material. The velocity of reduction depends primarily upon the strength of the depolarizer, which finds expression in its oxidation potential. Now, since the establishment of equilibrium requires time, it is conceivable that the same action may be produced by a weaker depolarizer if the condition of equilibrium is attained sooner owing to cathode action. Consequently, the power of any cathode to reduce, and of any substance to suffer reduction, may not be fully expressed by decomposition point data.

All of Flaschner's electrolysis runs were regulated so that no hydrogen was evolved. It seems, however, fairly evident that aside from the effect of oxidation potential and of cathode catalysis, an important factor enters to determine how far a reduction may proceed—that is, the concentration of the hydrogen. The maintenance of one cathode potential during electrolysis, by gradually decreasing the current density, may, of course, keep the hydrogen present in a constant excess; but this definite excess of hydrogen will, after a time, enter into equilibrium with the other products in solution at the cathode, so that it is conceivable that a stage in the electrolysis may be

[28] l. c.

[29] This is borne out by Tafel, who prepared hydroxylamine by electrolysis of nitric acid at a mercury cathode. Zeit. anorg. Chem., **31**, 289 (1902).

reached where no further reduction will take place, since these masses of reaction products can exist unchanged in the presence of each other at the given electrode potential and constant excess of hydrogen. The work done by the current passing through this solution in equilibrium is not clear. Still, it is a fact that exact experiments, such as those of Flaschner, have failed to account satisfactorily for a goodly quantity of the electricity which has passed. This wasted current is probably mostly of the nature of a residual current; but this last explanation is nevertheless speculation. This effect of hydrogen concentration has, of course, been considered by the investigators cited above; it is touched upon here to show that Flaschner might have gotten a much larger reduction of hydroxylamine at a copper cathode if he had used a current density above the hydrogen evolution potential (in hydroxylamine solution), as will be shown below. This result, too, is predicted by his decomposition point measurements in Table III.

Section II.

Effect of Concentration of Sulphuric Acid upon the Yield of Ammonia and of Hydroxylamine at a Copper Cathode.

Experiments were carried out to confirm the earlier work, showing that the yield of ammonia from nitric acid in sulphuric acid solution at a copper cathode is greater in more concentrated sulphuric acid, while the reverse is true of the hydroxylamine yield. A small cathode, 2 sq. cm. in area, was used in the cell shown in Fig. 1, the cathode solution being contained in the porous cup P, held by the coiled lead pipe anode, which is immersed in dilute sulphuric acid. The total volume of cathode solution used was 100 c.c.; it contained 0.25 gr. potassium nitrate (KNO_3), and sulphuric acid, 50, 12.9 and 1.7 per cent., as indicated in Tables IV, V and VI, which give the cathode discharge from time to time during the course of electrolysis, together with the yields and conditions.

TABLE IV.

Discharge potential at a copper cathode; solution contains 0.250 gr. KNO_3 and 50 per cent. H_2SO_4.

Minutes.	Volts.	Minutes.	Volts.
0		59.5	+0.149
9	—0.134	62.5	+0.149
21.5	+0.015	138.5	+0.164
35.5	+0.045	168.5	+0.164

NOTES: Date, July 25, 1907; current, 1 ampere; temperature, 28° C. Yield: Ammonia, 33.2 per cent. of total nitrogen; hydroxylamine, 4.1 per cent.

TABLE V.

Discharge potential at a copper cathode; solution contains 0.250 gr. KNO_3 and 12.9 per cent. H_2SO_4.

Minutes.	Volts.	Minutes.	Volts.
0		98	+0.047
2.5	+0.017	128	+0.092
5	+0.017	200	+0.092
23	+0.017		

NOTES: Date, July 24, 1907; cathode, 2 sq. cm. in area; current, 1 ampere; temperature, 30° C.; time, 203 minutes. Yield: Ammonia, 27.2 per cent. of total nitrogen; hydroxylamine, 30 per cent.

TABLE VI.

Discharge potential at a copper cathode; solution contains 0.250 gr. KNO_3 and 1.7 per cent. H_2SO_4.

Minutes.	Volts.	Minutes.	Volts.
0	.....	45	+0.156
3	—0.063	99	+0.216
7	+0.086	133	+0.231
16	+0.116	148	+0.267
23.5	+0.141	...	.....

NOTES: Date, July 25th; cathode, 2 sq. cm. in area; current, 1 ampere; temperature, 31.6° C. Yield: Ammonia, 15.2 per cent. of total nitrogen; hydroxylamine, 37.4 per cent.

Discussion: Comparing the discharge potentials in Tables IV, V and VI with the respective yields, it is seen that a high yield of ammonia is accompanied by a low cathode potential. In Table VI the discharge potential has a value of —0.063 volt after three minutes, but in seven minutes the potential has risen to +0.086 volt, which is much higher than the value given in Table IV for 50 per cent. sulphuric acid after thirty-five minutes of electrolysis. Similarly, at the end of the reduction in Table VI, the potential was +0.267 volt, a value much higher than in either Table IV or Table V.

The nitrogen loss is 62.7 per cent. in Table IV, 42.8 per cent. in Table V, and 47.4 per cent. in Table VI, consequently, the higher yield of ammonia in Table IV is not secured by an efficient reduction of nitrate. The loss of nitrate by diffusion through the porous cup into the anode solution is relatively slight, especially as the endosmosis is toward the cathode in this cell. This is shown conclusively, too, by later experiments in this same cell, in which practically all of the original nitrogen added as nitrate was recovered, partly as ammonia and partly as hydroxylamine. The probability is that at this high current density, 50 amperes per sq. dm., the lost nitrate is broken down to nitrogen gas.

Thus, the conclusion of Tafel[30] is confirmed, that the ammonia yield increases with increased concentration of sulphuric acid at a copper cathode, and that the hydroxylamine, on the other hand, forms in greater quantity in dilute sulphuric acid. In addition, it is shown that a low cathode potential accompanies the higher yield of ammonia.

SECTION III.

Effect of Current Density upon the Yield of Ammonia and of Hydroxylamine from the Reduction of Nitrate at a Copper Cathode.

To determine the effect of current density, solutions of the same composition as that used in Table VI were electrolyzed

[30] l. c.

in the same cell (see Fig. 1), with different current strengths and cathodes of copper. This particular concentration of acid (1.7 per cent.) was used, since it is the same as that recommended by Easton,[31] and, too, with current density of 50 amperes per sq. dm. in Table VI, this solution gave a yield of only 15.2 per cent. of the total nitrogen as ammonia. This yield, together with those given below in Tables VII and VIII, shows clearly the increase in the ammonia yield as the current density is decreased. The discharge potentials taken during reduction are likewise of interest.

TABLE VII.

Discharge potential at a copper cathode; 100 c.c. solution contains 0.250 gr. KNO_3 and 1.7 per cent. H_2SO_4.

Minutes.	Volts.	Minutes.	Volts.
0	.....	56	—0.067
0.75	—0.140	98.5	—0.006
2	—0.140	104	+0.092
10.5	—0.140	135	+0.092
28.5	—0.140	167	+0.098
47	—0.086	...	.....

NOTES: Date, June 25, 1907; area of cathode, 100 sq. cm.; lead anode in sulphuric acid isolated by a porous cup; current, 1 ampere; temperature, 32° C.; time, 180 minutes. Yield: Per cent. of total nitrogen as ammonia, 53.3; per cent. as hydroxylamine, 46.6.

TABLE VIII.

Discharge potential at a copper cathode; 100 c.c. solution contains 0.250 gr. KNO_3 and 1.7 per cent. H_2SO_4.

Minutes.	Volts.	Minutes.	Volts.
0	—0.430*	10	—0.028
1.5	+0.002	96	—0.092
3.5	—0.028	1196	+0.176

* No current passing.

NOTES: Date, July 26-27, 1907; area of cathode, 100 sq. cm.; lead anode in sulphuric acid isolated by a porous cup; current,

[31] Jour. Am. Chem. Soc., **25**, 1042 (1903).

0.45 ampere; temperature, 31° C.; time, 1,196 minutes. Yield: Per cent. total nitrogen as ammonia, 51; per cent. as hydroxylamine, 37.2.

Thus it is seen that the current density must be kept low to secure a good yield of ammonia.

Section IV.

Effect of Temperature upon the Yield of Ammonia from Nitric Acid at a Copper Cathode.

To ascertain the effect of temperature upon the yield of ammonia, an experiment was carried out under the same conditions as those for a copper cathode in Tables VII and VIII, except that the temperature was maintained at slightly below 9° C. In this case, 51 per cent. of the total nitrogen was obtained as ammonia, and 37.2 per cent. as hydroxylamine. These yields are close to those obtained at 25° C., so it is clear that differences of a few degrees above or below 25° C. are of minor import in comparing the experimental data in this research. Table IX gives the discharge potentials taken during this electrolysis. They show the same general trend as those in the experiments at higher temperature.

Table IX.

Discharge potential at a copper cathode; temperature, 9° C.

Minutes.	Volts.	Minutes.	Volts.
0	—0.397*	60	+0.038
2	—0.263	80	+0.038
3	—0.188	95	+0.113
4	—0.084	132	+0.138
12.5	—0.062	141	+0.138
16	—0.055	155	+0.138
25	—0.040	166	+0.158
45	+0.035	180	+0.158

* No current passing.

Notes: Date, June 26, 1907; cathode, 100 sq. cm.; anode, lead in dilute sulphuric acid isolated by a porous cup; solution, 100 c.c., containing 0.25 gram potassium nitrate (KNO_3) and 1.7 per cent. sulphuric acid (H_2SO_4); time, 180 minutes. Yield: Per cent. of total nitrogen as ammonia, 51; as hydroxylamine, 37.20.

Section V.

Effect of Copper Sulphate upon the Yield of Ammonia.

A. At a copper cathode. Using the same form of cell as before—that shown in Fig. 1—a series of determinations was made to ascertain how the yield of ammonia varied with the quantity of copper sulphate in solution. Table X contains the cathode discharge potentials obtained during the electrolysis of three different solutions, whose content of copper sulphate ($CuSO_4.5H_2O$) was 0.05 gr., 0.15 gr., and 0.25 gr. respectively.

Table X.

Discharge potential at a copper cathode as affected by various quantities of copper sulphate in solution.

I. $CuSO_4.5H_2O$, 0.050 gr.		II. $CuSO_4.5H_2O$, 0.150 gr.		III. $CuSO_4.5H_2O$, 0.250 gr.	
Minutes.	Volts.	Minutes.	Volts.	Minutes.	Volts.
0	—0.445	0*	—0.460	0*	—0.476
0.5	—0.171	2	—0.209	3	—0.286
3.5	—0.165	4	—0.204	5.5	—0.227
6.5	—0.165	13	—0.178	8	—0.207
7.0	—0.165	20.5	—0.176	9	—0.182
11.5	—0.038	37	—0.076	10	—0.169
17.5	—0.002	55	+0.032	12.5	—0.131
28.5	—0.002	69	+0.012	16	—0.139
40.5	—0.002	82	+0.087	19	—0.116
45.5	+0.043	155	+0.142	23	—0.109
57.5	+0.088	180	+0.183	28	—0.109
65.5	+0.094	...	.....	36	—0.097
69	+0.147	...	.....	39	—0.079
72.5	+0.147	...	.....	42	—0.050
80.5	+0.212	...	.....	44	—0.043
95	+0.212	...	.....	48.5	—0.035
				52.5	—0.024
				55.5	—0.008
				62	+0.008
				77	+0.039
				87	+0.090
				91	+0.127
				95.5	+0.141
				103	+0.156
				112.5	+0.156
				143	+0.156
				153	+0.156
				175	+0.156

Notes: Column I. Date, June 27, 1907; area of cathode, 100 sq. cm.; lead anode in sulphuric acid isolated by a porous

cup; solution, 100 c.c., containing 0.25 gr. potassium nitrate (KNO_3), 0.05 gr. copper sulphate ($CuSO_4.5H_2O$), 1.7 per cent. sulphuric acid (H_2SO_4); current, 1 ampere; temperature, 24° C.; total time, 180 minutes. Yield: Per cent. of total nitrogen as ammonia, 63.9; as hydroxylamine, 27.6.

Column II. Date, June 27, 1907; cathode and anode same as for Column I; solution same as for Column I, but with 0.150 gr. copper sulphate ($CuSO_4.5H_2O$); current, 1 ampere; temperature, 24° C.; total time, 181 minutes: Yield: Per cent. of total nitrogen as ammonia, 71.6; as hydroxylamine, 23.4.

Column III. Date, June 28, 1907; cathode and anode same as for Column I; solution same as for Column I, but with 0.250 gr. copper sulphate ($CuSO_4.5H_2O$); current, 1 ampere; temperature, 25° C.; total time, 180 minutes. Yield: Per cent. of total nitrogen as ammonia, 77.6; as hydroxylamine, 10.4.

In addition to the above experiments, others were made without taking discharge potentials. Using the same cell, cathode, anode and conditions as given for columns I, II and III, 0.650 gr. copper sulphate ($CuSO_4.5H_2O$) in solution gave, at 27° C., a yield of 76.6 per cent. of the total nitrogen as ammonia, and 5.2 per cent. as hydroxylamine; and 1.500 gr. copper sulphate ($CuSO_4.5H_2O$) in solution gave, at 25° C., 78.7 per cent. of total nitrogen as ammonia, and 2.2 per cent. as hydroxylamine.

The discharge potentials given in Table IX show that the presence of copper sulphate in solution keeps the cathode potential at a low value. This effect is strongly marked for the first small quantity of copper sulphate added, more so than for the solutions containing larger quantities.

Comparing the yields in Tables VII and VIII, where no copper sulphate was present, with the above results, it is seen that by allowing copper to deposit continually upon the cathode, the yield of ammonia may be increased from 53.3 per cent. of the total nitrogen present to 78.7 per cent., and the yield of hydroxylamine decreased from 46.6 per cent. to 2.2 per cent.

B. At an amalgamated copper cathode. The explanation has been offered[32] for this increased yield of ammonia in the presence of depositing copper, that it is due to the catalytic influence of the spongy copper. To test this, a series of determinations was

[32] By Tafel, l. c.

made, using an amalgamated copper cathode 100 sq. cm. in area, the other conditions remaining the same as in Table X, save that the quantity of copper sulphate in solution was varied.

Table XI.

Discharge potential at an amalgamated copper cathode as affected by various quantities of copper sulphate in solution.

I. No $CuSO_4$ Added.		II. No $CuSO_4$ Added.		III. $CuSO_4.5H_2O$ 0.650 gr.		IV. $CuSO_4.5H_2O$ 3.000 gr.	
Minutes.	Volts.	Minutes.	Volts.	Minutes.	Volts.	Minutes.	Volts.
0	—0 443*	. . . . .	. . . . .	0	—0.460*	0	—0.487*
1.5	+0.417	5	+0.421	1.5	—0.370	2	—0.519†
4	+0.425	37	+0.547	2.5	—0.362	4	—0.461‡
6	+0.490	72	+0.540	5.5	—0.323	6	—0.469
11	+0.477	173	+0.582	11	—0.173	8	—0.454
35	+0.535	365	+0.582	22	—0.016	10.5	—0.418
46	+0.520			23	—0.016	13.5	—0.375
64	+0.535			29	—0.016	18	—0 339
77	+0.535			35	+0.099	24	—0 336
133	+0.520			36	+0.099	29	—0.289
173	+0.586			56.5	+0.113	31.5	—0.238
				62	+0.128	38	—0.174
				78	+0.186	40	—0.174
				90	+0.243	47	—0.158
				109.5	+0.243	50	—0 145
				126	+0.243	55	—0.060
				143	+0.287	61	—0.016
				159	+0.426	65	+0.071
				168	+0.471	68.5	+0.071
						74	+0 093
						90.5	+0.093
						104	+0.164
						116	+0.185
						141	+0.179

* No current passing.
† On holding down the key the potential rises to its former value—0.487 volt.
‡ This value—0.461 volt—remains as a steady polarization.

Notes: Column I. Date, July 2; area of amalgamated copper cathode, 100 sq. cm.; lead anode in sulphuric acid isolated by a porous cup; solution, 100 c.c., containing 0.250 gr. potassium nitrate (KNO_3) and 1.7 per cent. sulphuric acid (H_2SO_4), but with no copper sulphate added; current, 1 ampere; temperature, 26° C.; total time, 180 minutes. Yield: Per cent. of total nitrogen as ammonia, 20.8; as hydroxylamine, 27.6.

Column II. Date, July 2, 1907; cathode and anode same as for Column I; current, 1 ampere; temperature, 27° C.; total time, 365 minutes. Yield: Per cent. of total nitrogen as ammonia, 53.8; as hydroxylamine, 25.5.

Column III. Date, July 3, 1907; cathode and anode and solution same as for Columns I and II, save that 0.650

gram copper sulphate ($CuSO_4.5H_2O$) was added; current, 1 ampere; temperature, 25° C.; total time, 181 minutes. Yield: Per cent. of total nitrogen as ammonia, 70.5; as hydroxylamine, 21.2. The cathode was left fairly smooth at the end of the run, the only roughness being occasioned by little grains of amalgamated copper, which were easily washed off by a wash-bottle jet of water. The porous cup contained considerable amalgamated copper which evidently had been deposited, and then had rolled down the cathode and fallen off.

Column IV. Date, July 5, 1907; cathode and anode and solution the same as for Column III, save that 3 grams $CuSO_4.5H_2O$ was added; current, 1 ampere; temperature, 22° C.; time, 180 minutes. Yield: Per cent. of total nitrogen as ammonia, 82.1; as hydroxylamine, 5.2.

The discharge potentials in Columns I and II, where no copper sulphate was used, check very well. In this case, the yield of ammonia is increased from 20.8 per cent. to 53.8 per cent. by increasing the time, while the yield of hydroxylamine is very nearly the same. In view of the tendency of hydroxylamine to form at a mercury cathode, this result is only to be expected. The effect of the copper deposition upon the yield of ammonia is striking, and is paralleled by the maintenance of a low cathode potential, just as at a copper cathode. It seems then that the formation and catalytic action of spongy copper upon the cathode is not a prime factor in the increased yield of ammonia. The cathode surface presented to the solution was smooth, the few small granules adhering to it being so amalgamated as to add nothing to its roughness.

An experiment similar to those given in Table XI was allowed to run over night, and the sulphuric acid added became exhausted, so that the solution gave alkaline reaction. The discharges at the cathode in the solution, taken as it passed from acid to alkaline solution, are interesting.

TABLE XII.

Discharge potential of an amalgamated copper cathode in acid and in alkaline nitrate solutions.

Minutes.	Volts.	Minutes.	Volts.
0	—0.427*	68	+0.561
4	+0.561	1114	+1.371†
6.5	+0.554	....	+0.459‡
28	+0.577	....	.....

* No current passing.
† Solution alkaline.
‡ + 5 c.c. H_2SO_4 solution, equivalent to 0.857 gram H_2SO_4.

NOTES: Date, July 1-2, 1907; cathode area, 100 sq. cm.; anode lead in sulphuric aid isolated by a porous cup; solution, 100 c.c., containing 0.250 gr. potassium nitrate (KNO_3) and 1.7 per cent. sulphuric acid (H_2SO_4), but no copper sulphate; current, 1 ampere. Yield: Per cent. of total nitrogen as hydroxylamine, 0.3; ammonia not determined, as some had probably volatilized.

This high discharge potential of +1.371 volts is due to the amalgam formed at the cathode, of potassium and ammonium.

In Table XIII is given a summary of the yields of ammonia and of hydroxylamine at copper and at amalgamated copper cathodes, as affected by varying quantity of copper sulphate in solution.

TABLE XIII.

Effect of copper sulphate in solution upon yield of ammonia and of hydroxylamine.

Temperature.	$CuSO_4.5H_2O$.	Nitrogen as Ammonia.	Nitrogen as Hydroxylamine.
COPPER CATHODE.			
	Grams.	Per Cent.	Per Cent.
25°	0.000	53.3	46.6
25°	0.000	50.3	33.9
9°	0.000	51	37.2
25°	0.050	63.9	27.6
25°	0.150	71.6	23.4
25°	0.250	77.6	5.2
27°	0.650	76.6	2.2
25°	1.500	78.7	2.2
AMALGAMATED COPPER CATHODE.			
26°	0.000	20.8*	27.6*
27°	0.000	53.8†	25.5†
25°	0.650	70.5	21.2
22°	3.000	82.1	5.2

* Time, 180 minutes. † Time, 365 minutes.

To show the effect of a mercury cathode upon the yield of ammonia and of hydroxylamine, an experiment was carried out as follows: Mercury was poured into a glass beaker of some 250 c.c. capacity, electrical connection with the mercury being secured by a platinum point fused into a glass tube, which was then filled with mercury and placed in the beaker. The platinum anode dipped directly into the solution, no porous cup being used, since it appeared from the work of Easton[33] and of Ingham[34] that no loss of nitrogen was to be feared at the anode. The discharge potential at the anode was taken here, as well as that at the cathode. These values are given in Table XIV.

TABLE XIV.

Discharge potentials at mercury cathode and platinum anode during reduction of potassium nitrate in sulphuric acid solution.

Anode.		Cathode.	
Minutes.	Volts.	Minutes.	Volts.
0	—0.658*	0	—0.739*
0	—0.864†	0	—0.786†
...	.....	1.5	—0.027
...	.....	3.5	+0.058
...	.....	6	+0.029
10	—1.980	9	+0.048
...	.....	33	+0.114
...	.....	51	+0.100
...	.....	68	+0.082
...	.....	96	—0.021
...	.....	100	—0.013
116	—1.969	118	—0.013
...	.....	133	+0.019
...	.....	144	+0.029
194	—1.924	198	—0.021
...	.....	210	—0.021
240	—1.957	232	—0.027

* KNO_3 alone, no H_2SO_4 present.
† H_2SO_4 added, but no current passing.

NOTES: Date, July 23, 1907. Cathode, mercury 31.2 sq. cm. in area; anode, polished platinum foil, 20 sq. cm. in area; solution, 150 c.c., containing 0.5 gr. potassium nitrate (KNO_3), and 1.7 per cent. sulphuric acid (H_2SO_4); current, 0.70 ampere;

[33] Jour. Am. Chem. Soc., **25**, 1042 (1903).
[34] Ibid., **26**, 1251 (1904).

time, 240 minutes; temperature, 31° C. Yield: Per cent. of total nitrogen as ammonia, 18.3; as hydroxylamine, 20.

The effect of acidifying the solution is to lower slightly the cathode single potential, but the values in both neutral (—0.739 volt) and acid solution (—0.786 volt) are considerably below the lowest value given by copper in this solution, which varies from —0.4 to —0.5 volt, a difference of some 0.3 volt. Within 1.5 minutes this cathode polarization at mercury has risen to —0.027 volt, and in 3.5 minutes it is at —0.058 volt, from which it falls slightly, and then rises to a maximum of +0.114 volt after 33 minutes, and then falls again to fairly steady polarization of —0.02 volt, as might be expected with 20 per cent. of hydroxylamine still in solution.

The anode discharge remains fairly constant throughout the experiment, only a slight fall of 0.023 volt being noticed between the beginning and end of the run.

C. Conditions recommended for quantitative conversion of nitrate to ammonia, using copper sulphate.

Easton[35] has confirmed the work of Vortmann; when a platinum dish is used as cathode, the copper in solution is deposited in a compact coating, and the conversion of nitrate to ammonia is quantitative; but when a copper plate 100 sq. cm. in area was suspended in the solution and used as cathode, the precipitated copper was spongy, did not adhere well, and consequently was difficult to wash. The per cent. of nitrogen converted from nitrate to ammonia varied from 13.04 to 13.44, whereas the theoretical yield is 13.86 per cent. Lead plates 100 sq. cm. in area were also tried, but the copper was precipitated upon them in very unsatisfactory form. They were also attacked, and the nitrate was never completely reduced when they were employed. No better success was met with mercury cathodes, while nickel (36 sq. cm. area) proved very satisfactory. Copper nitrate, electrolyzed alone, without copper sulphate, yielded 11.52 and 11.35 per cent. of nitrogen (theoretical yield 11.59) as ammonia. Silver nitrate was not completely reduced to ammonia until after the addition of an equal amount of copper sulphate. The time required to reduce 0.5 gram potassium nitrate (KNO_3) with 1 ampere was 2.5 hours.

[35] Jour. Am. Chem. Soc., **25**, 1042 (1903).

In a paper prepared for the technical public, Easton[36] has recommended the following conditions: "Dissolve the salt or acid in water, dilute to 150 c.c., and add the sulphuric acid. A beaker glass with a *copper plate* for the cathode is the most convenient form to use. The cathode should have at least 100 sq. cm. surface, counting both sides. The larger the cathode, the better the deposition of copper, although the size has no effect on the reduction. It should be in the form of a half-cylinder, as shown, and must not cut off any of the solution. (See Fig. 2.) The anode must be of platinum wire, as shown. Its size has no effect upon the reduction. Cover the glass, to prevent spattering, and connect the current. The use of about 3 amperes is recommended, and this will reduce 0.07 gram of nitrogen (equal to 0.5 gram of potassium nitrate) in one and one-fourth hour." Easton here recommends the form of cathode which in the first paper (1903) was shown to give results departing from the theoretical by 6 per cent.; he gives no new data or explanation with this recommendation.

Ingham[37] has reduced the time required for reduction of nitrate to ammonia by use of a rotating anode and higher current density, the other conditions being practically those suggested by Vortmann,[38] *i. e.*, the unknown nitrate solution is acidulated with a known quantity of standard sulphuric acid, a known weight of copper sulphate ($CuSO_4.5H_2O$) added, and the acid remaining unneutralized by ammonia at the end of the electrolysis is titrated with standard alkali. The anode used was a platinum wire 1 mm. in diamter, bent into a spiral 2 inches in diameter. The plane of the spiral was nearly flat, but slightly depressed in the center, in dish form, to conform approximately to the figure which the surface of the liquid assumes in the dish while agitated. The amount of liquid in the dish was usually about 125 c.c. As the stirring of the electrolyte caused the level of the liquid to rise at the walls of the dish, the amount of cathode surface exposed varied constantly, but was kept as near 100 sq. cm. as was possible under the circumstances. A current of 4 amperes gave a yield of 13.83 per cent. of the nitrogen as ammonia, whereas the theoretical yield is 13.86 per cent., in 30 minutes.

[36] Chemical Engineer, **1**, 144 (1905).
[37] Jour. Am. Chem. Soc., **26**, 1251 (1904).
[38] l. c.

Several reductions were carried out under the conditions mentioned by Easton, as follows:

(A) Date, June 28, 1907. Solution, 150 c.c., containing 0.500 gr. KNO_3, 0.500 gr. copper sulphate ($CuSO_4.5H_2O$), and 1.7 per cent. sulphuric acid (H_2SO_4); cathode, copper, 100 sq. cm. in area; anode, polished platinum wire, about 1 sq. cm. area; current, 1 ampere; time, 181 minutes; temperature, 30° C. Yield: Per cent. of total nitrogen as ammonia, 85.8; as hydroxylamine, 6. Here, with a high yield of ammonia, the cathode potential remains low throughout the electrolysis, as shown in Table XV.

TABLE XV.

Discharge potential at a copper cathode during the reduction of nitrate under Easton's conditions.

Minutes.	Volts.	Minutes.	Volts.
0	—0.488*	16	—0.182
3.5	—0.319	2.3	—0.102
5	—0.326	34	—0.102
7.5	—0.204	156	—0.102
9	—0.207	164.5	—0.087
11	—0.175	...	.....

* No current passing.

(B) Date, July 5, 1907. Solution, cathode and anode the same as in experiment (A); current, 1 ampere; time, 197.5 minutes; temperature, 30° C. Yield: Per cent. of total nitrogen as ammonia, 84.3; as hydroxylamine, 2.

(C) Date, July 5, 1907. A duplicate experiment run in series with experiment (B). Yield: Per cent. of total nitrogen as ammonia, 83.6; as hydroxylamine, 2.

(D) Date, July 6, 1907. Solution and cathode same as in experiments (A) and (B), but with anode of polished platinum, 20 sq. cm. in area; current, 1 ampere; time, 226 minutes; temperature, 26° C. Yield: Per cent. of total nitrogen as ammonia, 86.7; as hydroxylamine, 0.9.

(E) Date, July 6, 1907. A duplicate experiment run in series with experiment (D). Yield: Per cent. of total nitrogen as ammonia, 86.3; as hydroxylamine, 0.8.

(F) Date, July 11, 1907. Solution, cathode and anode the same as in experiments (D) and (E). Current, 1 ampere; time, 240 minutes; temperature, 31° C. Yield: Per cent. of total nitrogen as ammonia, 88.9; as hydroxylamine, 1.1. The anode and cathode discharge potentials are given below in Table XVI.

TABLE XVI.

Discharge potentials at anode and cathode during reduction of nitrate under Easton's conditions.

Anode.		Cathode.	
Minutes.	Volts.	Minutes.	Volts.
0	—0.874*	0	—0.472*
6	—2.007	3	—0.425
9	—1.999	26	—0.368
21	—1.905	34	—0.337
30	—2.007	42	—0.297
48	—2.010	60	—0.155
55	—2.007	77	—0.098
81	—2.012	99	—0.066
104	—1.992	121	—0.052
115	—2.007	134	—0.049
145	—1.997	192	—0.014
184	—1.997	...	.....
240	—1.997	...	.....
Permanent polarization.	—0.187	Permanent polarization.	—0.457

* No current passing.

Comparing experiments (D), (E) and (F), it appears that the yield of ammonia is increased slightly by electrolyzing for a longer time, but, as will be shown later, passing the current for a number of hours failed to convert the nitrate completely to ammonia.

(G) Date, July 12, 1907. Solution and cathode same as in experiment (F). Anode, polished platinum wire 0.5 sq. cm. in area; current, 1 ampere; time, 195 minutes; temperature, 28° C. Yield: Per cent. of total nitrogen as ammonia, 86.2; as hydroxylamine, 1.76. Anode and cathode discharge potentials are given in Table XVII.

TABLE XVII.

Discharge potentials at anode and cathode during reduction of nitrate under Easton's conditions.

Anode.		Cathode.	
Minutes.	Volts.	Minutes.	Volts.
0	—0.677*	0	—0.478*
1.5	—1.979	8	—0.446
3	—2.006	16	—0.426
6	—2.016	37	—0.389
13	—2.016	49	—0.357
47	—2.066	63	—0.296
66	—2.073	92	—0.125
82	—2.055	109	—0.096
142	—2.042	135	—0.096
172	—2.027	138	—0.082
....	.....	178	—0.011

* No current passing.

The yield in experiment (G) is very close to those in experiments (B), (C), (D) and (E), and the discharge potentials at the cathode, too, are of the same order. The effect of current density is evident in the lower values for the anode polarization, where the small platinum anode was used. This, together with the fact that the highest yield of ammonia was obtained in experiment (F), where a polished platinum anode 20 sq. cm. in area was used, suggests that the general statement made by Easton and others, that the area of the anode is without effect upon the yield, may not hold rigidly. This will be considered in detail below.

(H) Date, July 15, 1907. An experiment was carried out to see whether a great excess of copper sulphate in solution might not increase the yield of ammonia, the other conditions being the same as in the experiments (A)-(G), above—cathode, copper, 100 sq. cm. in area; anode, polished platinum, 20 sq. cm. in area; current, 1 ampere; time, 180 minutes; temperature, 30° C.; weight of copper sulphate ($CuSO_4.5H_2O$) added, 5.000 gr. Yield: Per cent. of total nitrogen as ammonia, 79.7; as hydroxylamine, 2.5. The copper was not all deposited from solution during this run. It seems evident, from this result and from those of Ingham,[39] that an excess of copper sulphate

[39] l. c.

($CuSO_4.5H_2O$) is only not beneficial, but actually decreases the yield of ammonia. There is a ratio of hydrogen to copper deposited at the cathode which favors the reduction to ammonia. Ingham found that where too much copper sulphate had been added, the yield of ammonia was increased by adding sulphuric acid—that is, by increasing the ratio of hydrogen to copper depositing at the cathode.

(I) Date, August 1, 1907. A copper anode 33 sq. cm. in area was used in this experiment, the cathode, solution, and other conditions being the same as in experiments (A)-(H), above. Current, 1 ampere; time, 190 minutes; temperature, 30° C. Yield: Per cent. of nitrogen as ammonia, 57.5; as hydroxylamine, 2. Anode and cathode discharge potentials are given in Table XVIII, below.

TABLE XVIII.

Discharge potential at copper anode and copper cathode during reduction of nitrate under Easton's conditions.

Anode.		Cathode.	
Minutes.	Volts.	Minutes.	Volts.
0	—0.530*	0	—0.519*
0	—0.467†	0	—0.463†
4.5	—0.475	2.5	—0.239‡
8.5	—0.580	....	.....
Perm. Polarization	—0.540†	7.5	—0.386
17.5	—0.583	11.5	—0.245
39.5	—0.664	15.5	—0.245
67.5	—0.725	20.5	—0.491
108.5	—0.774	40.5	—0.464
156.5	—0.768	64.5	—0.477
188.5	—0.567	103.5	—0.505
....	.....	158.5	—0.496
....	.....	184.5	—0.533

* No current passing; solution neutral KNO_3 0.500 gr., $CuSO_4.5H_2O$ 0.500 gr. in 150 cc.

† No current passing; solution 0.500 gr. KNO_3, 0.500 gr. $CuSO_4.5H_2O$, with 1.7 per cent. H_2SO_4.

‡ A little gas was continually evolved at the edges of the cathode from the beginning of the experiment. No liberation of gas was observed at the anode.

This low yield of ammonia (57.5 per cent.) obtained in experiment (I), using a copper anode, emphasizes the necessity of maintaining the proper ratio between the copper depositing and the hydrogen available for reducing. The drop in the

cathode discharge (Table XVIII) after a diffusion of solution has been set up, is due to gradual increase in the quantity of copper depositing. This drop indicates, too, that the mere maintenance of a low electrode potential will not effect complete reduction of nitrate to ammonia.

Turrentine[40] has shown that a copper anode dissolving in nitric acid reduces the acid chiefly to nitric oxide (NO) when a copper salt is present in the solution; and when practically no copper is dissolved, the main reduction product is NH_3. This work suggests another reason why the yield of ammonia is low—that is, the copper anode does not simply dissolve and furnish copper sulphate and nitrate, but rather, produces a complicated reaction which involves the reduction of the nitrate, and possibly a loss of nitrogen as gaseous oxide, or even free nitrogen. The drop in the anode discharge as the electrolysis proceeds, and the subsequent rise in value to nearly its initial single potential confirms this view. The gas evolved at anode and cathode will be considered in a later section.

(J) Date, September 27, 1907. To determine the effect of the compactness of the copper coating upon the yield of ammonia, an experiment was carried out, using Easton's conditions with slight modification; cathode, platinum dish having an effective reducing area of 45 sq. cm.; anode, polished platinum wire, 3 sq. cm. in area. Solution, 50 c.c., containing 0.300 gr. potassium nitrate (KNO_3), 0.300 gr. copper sulphate ($CuSO_4.5H_2O$), and 1.7 per cent. sulphuric acid (H_2SO_4); current, 0.45 ampere; time, 1,170 minutes; temperature, 22° C. Yield: Per cent. of total nitrogen as ammonia, 82; as hydroxylamine, 0.03. Discharge potential from anode at end of run, —1.989 volt; from cathode, —0.016 volt. The current density here is 1 ampere per sq. dm., as in the experiments (A)-(I); the time is amply sufficient for reduction; the ratio of deposited copper to hydrogen is the same as recommended by Easton, but the yield of ammonia is lower than before. The very low content of hydroxylamine suggests that the reduction process was completed, and that a small quantity was formed by oxidation at the anode. The loss of nitrogen may be a loss from the system in the form of free nitrogen and gaseous oxides.

[40] Trans. Am. Electrochem. Soc., **10**, 49 (1906).

(K) Using the same platinum dish as cathode, but with a different strength of solution, another run was made. Solution, 75 c.c., containing 0.500 gr. potassium nitrate (KNO_3), 0.500 gr. copper sulphate ($CuSO_4.5H_2O$), and 1.7 per cent. sulphuric acid (H_2SO_4). Anode, polished platinum, 3 sq. cm. in area; effective cathode surface, about 65 sq. cm.; current, 1 ampere; time, 1,101 minutes; temperature, 20° C. Yield: Per cent. of total nitrogen as ammonia, 78.7; as hydroxylamine, 1.

(L) Date, October 9, 1907. Solution, 100 c.c., containing 0.500 gr. potassium nitrate (KNO_3), 0.500 gr. copper sulphate ($CuSO_4.5H_2O$), and 1.7 per cent. sulphuric acid (H_2SO_4); cathode, platinum dish having an effective reducing area of about 75 sq. cm.; anode, platinum wire 3 sq. cm. in diameter; current, 1 ampere; time, 182 minutes; temperature, 25° C. Yield: Per cent. of total nitrogen as ammonia, 81.5; as hydroxylamine, 1.4.

Ulsch's method. Several reductions were made according to the directions given by Ulsch.[41] Solution, 20 c.c., containing 0.400 gr. potassium nitrate (KNO_3) in 0.5 N sulphuric acid. Cathode, copper wire 1 mm. in diameter and 2 meters long, wound spirally to fit into a test tube of 2.2 cm. internal diameter. The copper spiral was oxidized by heating red hot and cooling in the air. Anode, a platinum wire, 6 cm. long and 0.5 mm. in diameter, placed axially inside the copper spiral and reaching nearly to the bottom of the test tube. The test tube was kept cool by immersion in running water, as shown in Fig. 6.

(N) Solution, anode and cathode as described above. Current, 1.25 ampere; time, 61 minutes; temperature, 15° C. Yield: Per cent. of total nitrogen as ammonia, 85; as hydroxylamine, 3.5. The current passed for 45 minutes before any hydrogen was liberated in bubbles at the cathode. A duplicate run gave: Ammonia, 86 per cent.; hydroxylamine, 3.7.

(O) Solution, anode and cathode the same as in experiment (N). Current, 0.9 ampere; time, 213 minutes; temperature, 15° C. Yield: Per cent. of total nitrogen as ammonia, 84.3; as hydroxylamine, 0.1. At the end of the electrolysis, the cathode discharge was —0.08 volt, having remained at this value for some twenty minutes.

[41] l. c.

At the beginning of an experiment, before any current had passed, the single potential of the copper spiral in this solution was —0.494 volt, at 20° C., and that of the platinum anode, —0.603 volt. This reading was taken after the copper spiral had stood for ten minutes in this solution, and every trace of oxide had disappeared from the surface of the copper. After standing 35 minutes longer, the cathode single potential was still —0.494 volt. No electrolysis was made with this clean copper spiral until it had been again oxidized. In the experiments (N) and (O) above the e. m. f. was applied to the cell before any of the solution was run in, so that this solution of the oxide by nitric acid before any current passed might be avoided.

(P) Current, 1.25 ampere; time, 120 minutes. Yield: Per cent. of total nitrogen as ammonia, 82.8; as hydroxylamine, 1. During the period of 45 minutes before any gas was liberated at the cathode, 3,412 coulombs passed through the cell when the current was 1.25 amperes. For the complete reduction of 0.4 gram potassium nitrate (KNO_3) to ammonia, only 3,055 coulombs are needed when all the hydrogen liberated is used in the reduction. This shows a waste of some 360 coulombs, or about 0.0037 gram hydrogen. This waste of current in reduction below the current density at which hydrogen is liberated in visible bubbles has been noted by Flaschner[42] and others, and is attributed to diffusion of dissolved anode and cathode gases, which produce the so-called residual current.

(Q) *Rotating cathode of copper-plated platinum.* Solution, 150 c.c., containing 0.500 gr. potassium nitrate (KNO_3), 5.000 gr. copper sulphate ($CuSO_4.5H_2O$), and 1.7 per cent. H_2SO_4; cathode area, 20 sq. cm.; anode, polished platinum, 0.5 sq. cm. in area; current, 1 ampere; time, 183 minutes; temperature, 30° C. Speed of cathode, about 200 revolutions per minute. Yield: Per cent. of total nitrogen as ammonia, 68; as hydroxylamine, 1.45. Time required to deposit all copper from solution, 101 minutes. Anode and cathode discharge potentials are given in Table XIX.

[42] l. c. and references there cited.

Table XIX.

Discharge potential at rotating copper-plated cathode, and at platinum anode during reduction of nitrate in sulphuric acid solution.

Anode.		Cathode.	
Minutes.	Volts.	Minutes.	Volts.
0	.....	69	—0.506
22	—1.897	75	—0.503
57.5	—1.943	80	—0.485
174	—1.950	82	—0.482
		85	—0.479
Cathode.		88	—0.482
		94	—0.475
0	.....	101	—0.467†
6	—0.538	110	—0.448
8	—0.538	119	—0.334
12	—0.545	121.5	—0.273
13	—0.538	122.5	—0.260
16.5	—0.531	123	—0.235
22.5	—0.549	123.5	—0.221
25	—0.517	124.5	—0.221
31	—0.538	126	—0.206
32	—0.541	132	—0.093
33	—0.541	139	—0.045
37	—0.531	143	—0.042
43	—0.527	149	—0.039
53	—0.518*	156	—0.030
63	—0.508	164	—0.034
65	—0.506	173	—0.039
67	—0.506		

* Permanent polarization with external e. m. f. taken from cell.
† Copper all deposited from solution.

The anode discharge potential is slightly above that in the solutions, which were not stirred, as might be expected with a more continuous supply of anode solution. The cathode discharge is lower than any obtained with the unstirred solutions, although the current density is five times greater than that used in experiments (A) to (I), inclusive.

Current available for reduction: Five grams copper sulphate ($CuSO_4.5H_2O$) contain 1.2733 grams copper, which requires some 3,867 coulombs for its deposition, if 96,600 coulombs be taken as the electrochemical unit. Now, during the 101 minutes actually required to deposit all the copper from solution, 6,060 coulombs passed through the cell, leaving 2,193 coulombs for

reducing nitrate. To reduce 0.500 gr. potassium nitrate (KNO_3) completely to ammonia requires 3,818 coulombs. Therefore, if this complete reduction is taking place at the cathode, there will be needed 1,625 coulombs—that is, 42.3 per cent. of the nitrate would remain to be reduced, supposing no hydroxylamine or nitrite is formed. The electrolysis was continued 82 minutes after the copper had been all deposited, giving 4,920 coulombs, a little over three times the quantity necessary to complete the reduction. As only 68 per cent. of the total nitrogen was recovered as ammonia, corresponding to 2,600 coulombs, the current efficiency of this reduction is 36.6 per cent. with respect to ammonia. Similarly, the current efficiency for hydroxylamine is 0.57 per cent.

In experiment (H), above, where the same quantity of copper sulphate ($CuSO_4.5H_2O$) was used and no attempt made to stir the solution, 79.7 per cent. of the total nitrogen was reduced to ammonia. Here the current was passed for 180 minutes, giving 10,800 coulombs, but during this time not all the copper was deposited, so the quantity of electricity available for nitrate reduction was slightly higher, and the yield, too, is higher for both ammonia and hydroxylamine than in experiment (Q), but the current efficiency cannot be calculated, since some copper remained in the solution, and the actual weight deposited is not known. In experiment (F), using only 0.500 gr. copper sulphate ($CuSO_4.5H_2O$), the quantity of electricity required to deposit the copper is 387 coulombs. The current, 1 ampere, passed for 240 minutes, giving 14,400 coulombs. This leaves 14,013 coulombs available for reduction of nitrate; of this, 3,394 were used in reducing to ammonia (88.9 per cent. yield), a current efficiency of 24.2 per cent.; similarly, for hydroxylamine the current efficiency is 0.22 per cent.

These considerations emphasize the necessity of maintaining a proper ratio between the hydrogen and the copper depositing at the cathode to secure the best yield of ammonia.

Section VI.

Effect of the Cathode Metal upon the Reduction of Nitrate.

(A) *Reduction in acid solution.* Tafel[43] gives the following series, showing the yield of hydroxylamine, in per cent. of total

[43] l. c.

nitrogen, obtained by reducing nitric acid in 50 per cent. sulphuric acid solution at various cathodes, using a current density of 24 amperes per sq. dm.; lead, 31.8; smooth copper, 11.5; spongy copper, 1.5; smooth silver, 14.4; smooth nickel, 36.8; smooth tin, 51.7 to 45.8; smooth carbon, 25.2; smooth cadmium, 39.1; smooth aluminum, 16.8; smooth bismuth, 59.4. The solution contained 0.4 gr. HNO_3 and was ice-cooled. The time of electrolysis varied from two to three hours. Lead, tin and copper amalgams gave from 60 to 70 per cent. of hydroxylamine, the effect of the mercury, which favors the reduction to hydroxylamine, predominating. Tafel gives no discharge potentials.

Mercury cathode. In Section V, Table XIV, discharge potential measurements are given for a mercury cathode during the reduction of nitrate in sulphuric acid solution. The yield of hydroxylamine here is only 20 per cent. of the total nitrogen, together with 18.3 per cent. of ammonia. It should be remembered that Tafel's higher yield of hydroxylamine was obtained in 50 per cent. sulphuric acid, with a much higher concentration of nitrate (0.4 to 0.6 gr. nitric acid [HNO_3] in 20 c.c. of solution), as well as at a current density some 500 per cent. greater than that used here.

The low current and low concentrations were adhered to in this work, in order to secure results comparable with those given above.

Platinum cathode. Solution, 150 c.c., containing 0.500 gr. potassium nitrate (KNO_3) and 1.7 per cent. sulphuric acid (H_2SO_4); cathode, polished platinum, 58 sq. cm. in area; anode, polished platinum, 20 sq. cm. in area; current, 1.3 amperes for 180 minutes, giving a current density of 2.24 amperes per sq. dm.; the curent was then reduced to 0.7 ampere and allowed to pass all night, 882 minutes longer; temperature, 20° C. Yield: Per cent. of total nitrogen as hydroxylamine, 0.2; as ammonia, 4. The discharge potentials from the cathode are given in Table XX.

TABLE XX.

Discharge potential at polished platinum cathode during the reduction of nitrate in sulphuric acid solution.

Minutes.	Volts.	Minutes.	Volts.
0	—0.910*	9	—0 146
3	—0.153	26	—0.154
6	—0 189	37	—0 125

* No current passing.

The discharge at the cathode is higher than that found at a copper cathode, where the main product of reduction was ammonia.

Lead cathode. Solution, 100 c.c., containing 0.250 gr. potassium nitrate (KNO_3) and 1.7 per cent. sulphuric acid (H_2SO_4). Cathode, smooth lead, 100 sq. cm. in area; anode, lead, in dilute sulphuric acid, isolated by a porous cup; current, 1 ampere; time, 180 minutes; temperature, 27° C. Yield: Per cent. of total nitrogen as ammonia, 11.9; as hydroxylamine, between 85 and 90. The end point of the titration with permanganate was not sharp. The discharge at the cathode is given in Table XXI.

TABLE XXI.

Discharge potential at a lead cathode during the reduction of nitrate in sulphuric acid solution.

Minutes.	Volts.	Minutes.	Volts.
0	+0.058*	15	+0.242
1	—0.014	16.5	+0.245
2	+0.044	25	+0.246
2.5	+0.051	32	+0.271
3	+0.073	47	+0.278
3.75	+0.088	57.5	+0.300
4.5	+0.116	71.5	+0.300
5	+0.146	110.5	+0.315
9.5	+0.205	134.5	+0.331
10.5	+0.213	....	.....

* No current passing.

Thus, a high yield of hydroxylamine is seen to be accompanied by a high discharge potential at the cathode. From the standpoint of reaction velocity, this curve of cathode polarization

with time is interesting; the rate of change of the cathode potential may be very well expressed by the first order reaction velocity equation, $\frac{d\pi}{dt} = K(A - \pi)$, where π is the discharge potential; t, the time; A, the highest potential reached at the cathode, and K, a velocity constant.

Zinc cathode. (A) Solution, 100 c.c., containing 0.250 gr. potassium nitrate (KNO_3) and 1.7 per cent. sulphuric acid (H_2SO_4); cathode, smooth sheet zinc, 100 sq. cm. in area; anode, lead in dilute sulphuric acid, isolated by a porous cup (Fig. 1); current, 1 ampere; time, 45 minutes; temperature, 25.5° C. Yield: Per cent. of total nitrogen as ammonia, 22; as hydroxylamine, 54.7. Discharge potentials at the cathode are given in Table XXII.

TABLE XXII.

Discharge potential at a zinc cathode during the reduction of nitrate in sulphuric acid solution.

Minutes.	Volts.	Minutes.	Volts.
0	.....	39	+0.488
1.5	+0.418	45	+0.488
22	+0.488	..	.....

Zinc cathode. (B) To see if this low yield of ammonia is due to the short run of 45 minutes, a second experiment was carried out, using the same cell, solution, anode and cathode and current as before. Time, 180 minutes; temperature, 27° to 29° C. Yield: Per cent. of total nitrogen as ammonia, 28.5; as hydroxylamine, 70. The cathode discharge is given in Table XXIII.

TABLE XXIII.

Discharge potential at a zinc cathode during the reduction of nitrate in sulphuric acid solution.

Minutes.	Volts.	Minutes.	Volts.
0	+0.495*	73	+0.494
2	+0.495	114	+0.509
13	+0.470	131	+0.509
17.5	+0.495	161	+0.513
35	+0.494	177	+0.530
47	+0.494	180	+0.480†

* No current passing.

† A steady, permanent polarization of + 0.480 volt was observed at the end of the run, with the external E. M. F. taken off from the cell.

Electrolyzing for 135 minutes longer than in the first experiment with a zinc cathode has increased the yield of ammonia from 22.6 per cent. only to 28.5 per cent., while the hydroxylamine has gone up from 54.7 per cent. to 70. The discharge potential here in Table XXIII is slightly higher at times than in Table XXII.

Aluminum cathode. (A) Solution, 150 c.c., containing 0.375 gr. potassium nitrate (KNO_3) and 1.7 per cent. sulphuric acid (H_2SO_4). Cathode, smooth aluminum, 150 sq. cm. in area; anode, polished platinum, 20 sq. cm. in area; current, 1.3 amperes; time, 105 minutes; temperature, 28° C. Yield: Per cent. of total nitrogen as ammonia, 38.2; as hydroxylamine, 1.24. The cathode discharge potentials are given in Table XXIV.

TABLE XXIV.

Discharge potential at an aluminum cathode during the reduction of nitrate in sulphuric acid solution.

Minutes.	Volts.	Minutes.	Volts.
0	—0.093*	62	—0.042
4.5	—0.138	74	—0.050
6.5	—0.071†	81	—0.050
31	—0.057‡	96	—0.050

* No current passing.
† Stirring lowered the discharge to —0.128 volts at 9 minutes after the start.
‡ Stirring had no effect upon the discharge potential.

Aluminum cathode. (B) Solution, 100 c.c., containing 0.250 gr. potassium nitrate (KNO_3) and 1.7 per cent. sulphuric acid (H_2SO_4). Cathode, smooth aluminum, 100 sq. cm. in area; anode, lead in dilute sulphuric acid, isolated by a porous cup; current, 1 ampere; time, 792 minutes; temperature, 27° C. Yield: Per cent. of total nitrogen as ammonia, 55.7; as hydroxylamine, 16.6. The cathode discharge potentials are given in Table XXV.

TABLE XXV.

Discharge potentials at aluminum cathode during reduction of nitrate in sulphuric acid solution.

Minutes.	Volts.
0	—0.032*
1	+0.112
792	+0.105

* No current passing.

The yield of ammonia is increased from 38.2 per cent. to 55.7 per cent. by this long run; and the hydroxylamine likewise increases from 1.24 per cent. to 16.6. This renders it extremely improbable that hydroxylamine can be completely reduced at an aluminum cathode.

(B) *Reduction in alkaline solution.* Experiments were carried out, using copper, zinc and platinum cathodes, in alkaline solution, to ascertain the yields of hydroxylamine and of ammonia under conditions in other respects similar to those used above. Discharge potentials at anode and cathode were likewise taken. To insure against loss of ammonia by volatilization, the cell was closed by a rubber stopper, and a delivery tube conducted the mixed anode and cathode gases through a known solution of sulphuric acid contained in an absorption tube. This precaution, however, was found to be unnecessary.

Copper cathode. Solution, 150 c.c., solution containing 0.250 gr. potassium nitrate (KNO_3) and 4.433 gr. potassium hydroxide (KOH); cathode area, 100 sq. cm.; anode, polished platinum, 20 sq. cm. in area; current, 1 ampere; time, 233 minutes; temperature, 31° C. Yield: Per cent. of total nitrogen as ammonia, 16.6; as hydroxylamine, 4.4. No porous cup was used. The cell is shown in Fig. 3. Discharge potentials at anode and cathode are given in Table XXVI.

TABLE XXVI.

Discharge potential at platinum anode and copper cathode during reduction of nitrate in alkaline solution.

Anode.		Cathode.	
Minutes.	Volts.	Minutes.	Volts.
0	—0.401*	0	+0.010*
29	—1.268	9	+0.698
41	—1.281	24	+0.772
85	—1.322	73	+0.594
122.5	—1.333	81	+0.466
...	.....	120	+0.678

* No current passing.

The anode polarization is lower in alkaline solution than in the acid solutions studied above. A check experiment was made to determine the discharge potential of platinum as anode and as cathode in potassium hydroxide solution alone, of the strength used in this series at different current densities. The values obtained are given in Table XXVII.

TABLE XXVII.

Discharge potentials at platinum in potassium hydroxide (4.433 gr. KOH in 150 c.c. water) for different current densities.

Area.	Single Potential.	Discharge Potential.		Current.	Current Density per Sq. Dm.
		Anode.	Cathode.		
Sq. Cm.	Volts.	Volts.	Volts.	Amperes.	Amperes.
60	—0.402	—1.334	{ +0.638 +0.634	1.00	1.67
20	—0.328	—1.336	+0.635	1.00	5
2	—0.435	—1.332	.....	1.00	50

It will be seen that the anode values check well with those in Table XXVI, the effect of a reaction at the anode being evident in the higher discharge voltage, which falls to that of oxygen at the end of the run.

The polarization at the copper cathode shown during the reduction of nitrate in Table XXVI is high, higher than at a platinum cathode in potassium hydroxide solution, as shown

in Table XXVII, and here, too, with a high cathode potential we get a low yield of ammonia, only 16.6 per cent., after a run of some four hours. It is interesting to note that a copper cathode left one night in a portion of this same solution, after the electrolysis was finished, was oxidized, and gave a single potential of —0.224 volt; upon electrolyzing a few minutes, the oxide was reduced, and the single potential (not the discharge potential) was +0.025 volt, which is practically the same value as that given initially in Table XXVI, before any current had been passed through the solution.

Platinum cathode. Solution, 150 c.c., containing 0.250 gr. potassium nitrate (KNO_3) and 4.433 gr. potassium hydroxide (KOH); cathode area, 2 sq. cm.; anode, polished platinum, 60 sq. cm. in area; current, 1 ampere; time, 197 minutes; temperature, 26° C. Yield: Per cent. of total nitrogen as ammonia, 3.4; hydroxylamine, not determined. The anode and cathode discharge potentials are given in Table XXVIII.

TABLE XXVIII.

Discharge potential at platinum anode and cathode during reduction of nitrate in alkaline solution.

Anode.		Cathode.	
Minutes.	Volts.	Minutes.	Volts.
0	—0.458*	0	—0.355*
5	—1.315	2	+0.507
11	—1.396	15	+0.507
17	—1.411	31	+0.564
21	—1.381	43	+0.524
58	—1.411	98	+0.656
88	—1.411	185	+0.667
191	—1.393	....	.....
197	—0.484†	....	+0.171†

* No current passing.
† Permanent polarization at end of run.

The high current density of 50 amperes per sq. dm. was used here because the previous work by Ihle[44] showed that at platinum a high current density is needed to secure reduction to ammonia. The cathode polarization is again high, as it was in Table XXVI, for a copper cathode, its end value being higher than those given in Table XXVII, as would be expected with the higher

[44] l. c.

current density used here in Table XXVIII. The depolarizing effect of the nitric acid is more regularly shown here than for copper in Table XXVI, but the range of depolarization, some 0.16 volt, is less than at the copper cathode, where it is about 0.3 volt. The end value of the polarization at copper, too, is higher than at platinum.

The anode discharge in Table XXVIII is higher than that in either Table XXVI or XXVII, and remains fairly constant after the first few minutes.

Zinc cathode. Solution, 150 c.c., containing 0.250 gr. potassium nitrate (KNO_3) and 4.433 gr. potassium hydroxide (KOH); cathode area, 100 sq. cm.; anode, polished platinum, 2 sq. cm. in area; current, 1 ampere; time, 180 minutes; temperature, 29° C. Yield: Per cent. of total nitrogen as ammonia, 22.9; hydroxylamine, not determined. Discharge potentials at anode and at cathode are given in Table XXIX.

TABLE XXIX.

Discharge potential at zinc cathode and platinum anode during reduction of nitrate in alkaline solution.

Anode.		Cathode.	
Minutes.	Volts.	Minutes.	Volts.
0	—0.331*	0	+0.832*
	—0.303		+0.986
12.5	—1.353§	5.5	+1.012†
22	—1.339	8.5	+0.957
27.5	—1.339	16.5	+0.997
38.5	—1.295	19.5	+1.013
44	—1.322	28.5	+1.019
61.5	—1.273	32.5	+1.019
71.5	—1.322	34.5	+1.014‡
131	—1.265	46.5	+1.013
141	—1.265	49.5	+1.013
165	—1.290	53.5	+0.999
169	—1.290	72.5	+1.013
178	—1.290	96.5	+1.013
180	—0.440¶	98.5	+0.985
	—0.297	129.5	+0.890
		145.5	+0.948
		158.5	+0.948
		161.5	+0.951
		171.5	+0.951
		178.5	+0.951‖

* No current passing.
† Fairly steady polarization.
‡ Steady polarization of 0.929 volt, with external e. m. f. taken from cell.
‖ Permanent polarization.
§ Polarization rapidly falls on releasing applied e. m.f.
¶ Permanent polarization falling to —0.297 volt.

Comparing the cathode polarization given in the above Tables XXVI to XXIX with those of Nutton and Law, in Table II, in Section I, it is seen that the two sets of values are in good accord. Thus, at a current density of 0.75 ampere per sq. dm., Nutton and Law find a polarization of +0.5273 volt at a copper cathode in 5 per cent. potassium hydroxide with 50 per cent. ethyl alcohol; the value in Table XXV here is 0.678 volt for a current density of 1 ampere per sq. dm. Similarly, for zinc in 5 per cent. potassium hydroxide, at a current density of 0.7 ampere per sq. dm., the cathode discharge is +0.9818 volt, and at 1.7 ampere per sq. dm., it is +1.08 volt, according to Nutton and Law. Here in Table XXVIII, at a current density of 1 ampere per sq. dm., the cathode discharge is from +1.019 volt to +0.951 volt, showing the depolarizing action of the nitrate, and that this depolarization is relatively slight as compared to that observed in the case of a copper cathode in these solutions. The current density used for platinum in Table XXVII, 50 amperes per sq. dm., is tenfold higher than that given by Nutton and Law, who obtained a polarization of +0.6038 volt in 5 per cent. potassium hydroxide for a current density of 5 amperes per sq. dm. The value given in Table XXVII (+0.667 volt) is what might be expected at the higher current density.

The anode polarization given in Tables XXV to XXVIII indicate that an action upon the nitrogen compounds is taking place at the anode. The effect of current density is shown in the lower discharge potentials from a platinum anode at lower current density.

It is evident that much more work is needed to clear up the reactions during the reduction of nitrate in alkaline solution.

A summary of the yields of ammonia and of hydroxylamine at various cathodes in acid and in alkaline solution is given in Table XXIX.

Table XXX—Summary.

Yield of ammonia and of hydroxylamine from nitrate at various cathodes in acid and in alkaline solution.

Metal.	Current Density Per Sq. Dm.	Time.	Current.	KNO_3 Taken	Total Reduced Nitrogen Recovered			
					H_2SO_4 Solution.		KOH Solution.	
					As NH_3	As NH_2OH	As NH_3	As NH_2OH
	Amp.	Min.	Amp.	Grams.	Per Ct.	Per Ct.	Per Ct.	Per Ct.
Copper	1.00	180	1.00	0.250	53.3	46.6	. . .	. . .
Aluminum . .	1.00	792	1.00	0.250	55.7	16.6	. . .	. . .
	0.87	105	1.30	0.375	38.2	1.24	. . .	. . .
Zinc	1.00	45	1.00	0.250	22.6	54.7	. . .	. . .
	1.00	180	1.00	0.250	28.5	70	. . .	. . .
Mercury . . .	2.24	240	0.70	0.500	18.3	20	. . .	. . .
Lead	1.00	180	1.00	0.250	11.9	85 to 90	. . .	. . .
Platinum . . .	2.24	180	1.30	0.500	4.0	0.2	. . .	. . .
	1.21	882	0.70	. . .	. . .	. . .	. . .	. . .
Copper	1.00	233	1.00	0.250	. . .	. . .	16.6	4.4
Zinc	1.00	180	1.00	0.250	. . .	. . .	22.9	. . .
Platinum . . .	50.00	197	1.00	0.250	. . .	. . .	3.4	. . .

Section VII.

Examination of Gases Liberated at Anode and Cathode.

A solution containing 1.000 gr. potassium nitrate, 1 gr. crystallized copper sulphate ($CuSO_4.5H_2O$) and 5.145 gr. sulphuric acid (H_2SO_4), dissolved in 300 c.c., was electrolyzed in a cell with a copper cathode, 100 sq. cm. total area, and a platinum anode 0.5 sq. cm. in area. The gas evolved was allowed to accumulate in a glass tube inserted over each electrode, as shown in Fig. 4, removed from time to time and analyzed, as already described in the section devoted to analytical methods. The current passed was 0.7 ampere during 202 minutes.

In the first 120 c.c. of anode gas, 5.84 per cent. was not absorbed by alkaline pyrogallol; this is equivalent to 7.7 c.c. of nitrogen at 29.4° C. and 767.6 mm., and to 0.00877 gr. nitrogen, or 5.7 per cent. of the total nitrogen present.

The next 166 c.c. anode gas gave 15 c.c. of gas unabsorbed

at 29°, and 767.6 mm. = 9.05 per cent. by volume of gas not oxygen. The following fraction, 64.8 c.c. of gas, from the anode gave 8.8 c.c. gas unabsorbed by the pyrogallol at 31.2° and 767.2 mm., or 13.57 per cent. by volume of a gas presumably nitrogen. Finally, 53.6 c.c., the last portion of anode gas, was lost by accident, and its content of nitrogen can only be surmised. Judging from the foregoing portions of anode gas, it may have contained as much as 10 per cent. nitrogen by volume.

At the cathode, 59 c.c. of gas first evolved left 2 c.c. gas unabsorbed by palladium at 29.4° C. and 766.6 mm., equivalent to 3.39 per cent. of the gas, by volume. The rest of the collected cathode gas was lost by an accident. The solution was found to contain 60 per cent. of the nitrate nitrogen in the form of ammonia, while the permanganate required to oxidize the solution is equivalent to 0.9 per cent. of the total nitrogen as hydroxylamine.

In Table XXXI are given anode and cathode discharge potentials taken during this electrolysis. Following the table are notes stating the conditions and yields.

TABLE XXXI.

Anode and cathode discharge potentials.

Anode.		Cathode.	
Minutes.	Volts.	Minutes.	Volts.
0	—0.895	0	—0.477
5	—1.966	9	—0.462
56	—1.966	17	—0.342
88	—1.974	48	—0.313
117	—2.004	72	—0.222
		85	—0.200
		128	—0.158
		142	—0.172
		194	—0.079
	Total time	202	

NOTES: Date, July 16, 1907; cathode, copper, 100 sq. cm. in area; anode, polished platinum, 0.5 sq. cm. in area; aqueous solution, 300 c.c. in volume, containing 1.00 gr. $CuSO_4.5H_2O$, 1.000 gr. KNO_3, 1.715 per cent. H_2SO_4; current, 0.7 ampere;

temperature, 35° C. Yield: 60 per cent. of nitrogen as NH_3, 0.9 per cent. of nitrogen as NH_2OH. Approximately 25 per cent. of total nitrogen lost at anode.

A second experiment was made under the same conditions as the one above, and the gases collected and analyzed without accident. The discharge potentials and volumes of gas collected are given in Table XXXII, together with the volumes of anode and cathode gas remaining unabsorbed by pyrogallol and by palladium. The conditions and yields are given following the table.

A third run was made, using ten times the quantity of copper sulphate used in the two previous experiments, but here again an accident occurred. It seems best, however, to give the data obtained here for comparison with the other experiments, especially since the yields of ammonia and of hydroxylamine have already been determined at this concentration, and since here it is shown that even with so strong a solution of copper sulphate hydrogen gas is liberated at this current density during the reduction of a nitrate, and that some of this gas evolved is not absorbed by palladium, and evidently is nitrogen. The discharge potentials and volume of gas liberated at the anode are given in Table XXXIII, and the conditions follow.

TABLE XXXII.

Anode and cathode discharge potentials, together with the quantity of gas evolved, and its composition.

ANODE DATA.						CATHODE DATA.					
Discharge Potential.		Gas Liberated.				Discharge Potential.		Gas Liberated.			
		Total Time.	Total Gas.	Gas Evolved Per Min.	Gas Unabsorbed by Pyrogallol.			Total Time.	Total Gas.	Gas Evolved Per Min.	Gas Unabsorbed by Palladium.
Minutes.	Volts.	Minutes.	c.c.	c.c.	Per Cent.	Minutes.	Volts.	Minutes.	c.c.	c.c.	Per Cent.
0*	—0.704	3	7.7	2.2	. . . .	0*	—0 477	. . . .	. . . .	. . . .	. . . .
3	—1.924	15.5	41.7	2.83	. . . .	30	—0.378	. . . .	. . . .	. . . .	. . . .
38.5	—1.974	61.5	165.4	2.5	. . . .	55	—0.215	. . . .	. . .	. . . .	. . . .
48	—1.980	71	186.8	2.25	. . . .	60	—0 215	71.5	72.6	1.01	9.54
74	—1.994	110	272.0	2.23	4.95	73	—0.194	. . . .	. . . .	. . . .	. . . .
98	—1.994	140	348.0	2.62	. . . .	105	—0.158	138	173.4	1.51	3.8
160	—1.994	176.5	432.2	2.24	6.44	108	—0.230	177.5	238.2	1.64	3.86
229	—1.974	210.0	519.2	2 6	6.4	120	—0.222	234	366.2	2.26	6.52
269.5	—2.002	243.0	618.2	2.72	6.4	128	—0.222	270	476.4	3.06	3.96
270	. . . . .	270	695.4	2.76	4 66	153	—0.208	. . . .	. . . .	. . . .	. . . .
. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	210	—0.158	. . . .	. . . .	. . . .	. . . .
. . . .	. . . . .	. . . .	. . . .	. . . .	. . . .	264	—0.477	. . . .	. . . .	. . . .	. . . .
. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	270	. . . . .	270	. . . .	. . . .	. . . .

*No current passing.

NOTES: Date, July 18, 1907; cathode, copper, 100 sq. cm. in area; anode, polished platinum, 0.5 sq. cm. in area; aqueous solution, 300 c.c. in volume, containing 1 000 gram $CuSO_4.5H_2O$, 1.000 gram KNO_3, 1.715 per cent. H_2SO_4; current, 0.7 ampere; temperature, 31° C.; yield, 64 per cent. of nitrogen as NH_3; 1.6 per cent. of nitrogen as hydroxylamine; 26 3 per cent. of nitrogen given off at the anode; 18.8 per cent. of nitrogen given off at cathode.

TABLE XXXIII.

Anode and cathode discharge potentials, together with the quantity of gas evolved, and its composition.

Discharge Potential.				Gas Liberated at Anode.					
Anode.		Cathode.		Total Time.	Gas.	Gas Unabsorbed by Pyrogallol.	Gas Unabsorbed by Pyrogallol.	Total Gas Unabsorbed.	Total Oxygen.
Minutes.	Volts.	Minutes.	Volts.	Minutes.	c.c.	c.c.	Per Cent.	c.c.	c.c.
0*	—0.691	0	—0 508*	. . . . .	. . . . .	. . . . .	. . . . .	. . . . .	. . . . .
2	—1.977	7	—0.532	20.3	51.7	3.3	6.34	3.3	48.7
8.5	—1.996	9	—0.518	40	48.9	2.6	5 31	5.9	95.0
55	—2.004	36	—0.504	59	50.2	3.0	5.97	8.9	142.2
120	—1.996	49	—0.477	78	53.8	3.6	6.7	12.5	192.4!
151	—1.996	69	—0 413	95	50.0	7.9	15.73	20 4	234.5
200	—2.004	93	—0.519	109	53.2	10.1	18.95	30.5	277.6
. . . .	. . . . .	106	—0 519	124	55.8	Sample lost by accident		. . . . .	. . . . .
. . . .	. . . . .	118	—0 519	136	51.8	12.2	23.5	. . . . .	. . . . .
. . . .	. . . . .	154	—0.498	159	54.3	12.9	23.7	. . . . .	. . . . .
(Total)	. . . . .	170	—0.491	174	54.3	. . . . .	. . . . .	. . . . .	. . . . .
217	. . . . .	197	—0.491	198	55.4	. . . . .	. . . . .	. . . . .	. . . . .
. . . .	. . . . .	217	—0.504	217	54.3	32.4	52.3	. . . . .	. . . . .

*No current passing.

NOTES: Date, July 22, 1907; cathode, copper, 100 sq. cm. in area; anode, polished platinum, 0.5 sq. cm. in area; aqueous solution, 300 c.c. in volume, containing 10.00 gr. copper sulphate ($CuSO_4.5H_2O$), 1.000 gr. potassium nitrate (KNO_3), 1.715 per cent. sulphuric acid (H_2SO_4); temperature, 30° C. The beaker containing the solution broke after the current, 0.7-0.8 ampere, had passed for 78 minutes, as indicated by the exclamation point in the table. This allowed tap water from the cooling bath to mingle with the original solution; consequently, no yield of ammonia or of hydroxylamine could be gotten from the experiment. In a comparable experiment,[45] using half the quantities taken here—in 150 c.c. of solution—but with the same cathode material and area, anode, 20 sq. cm., polished platinum, and a current very little higher (1 ampere), the yield was 79.7 per cent. of total nitrogen as ammonia, and 2.5 per cent. of the nitrogen as hydroxylamine, for a run of 180 minutes. The copper was not all deposited from solution in this last experiment. Anode and cathode discharges were not taken here, so this set of data on the single potential discharge at these concentrations, as given above in Table XXXIII, is of value, even if the solution in which they were obtained did become contaminated and render a determination of the yields impossible. During the run in Table XXXIII, 6.4 c.c. gas was evolved at the cathode; of this, 0.4 c.c. was not absorbed by palladium, at 26.1° C. and 761.2 mm. It is evident that even with a large supply of copper sulphate in solution, hydrogen is evolved, and some nitrogen along with it. At the anode, too, nitrogen is set free.

A fourth experiment was made, using the same strength of solution and same electrodes and cell as in the first two experiments in this section, but with a weaker current. The data are assembled in Table XXXIV, and the conditions and yields follow.

[45] See Experiment H, Section V, p. 360.

TABLE XXXIV.

Anode and cathode discharge potentials, together with the quantity of gas evolved, and its composition.

ANODE DATA.							CATHODE DATA.						
Discharge Potential.		Gas Liberated.					Discharge Potential.		Gas Liberated.				
		Total Time.	Gas.	Gas Unabsorbed by Pyrogallol.	Total Gas Unabsorbed	Total Oxygen.			Total Time.	Gas.	Gas Unabsorbed by Palladium.	Total Gas Unabsorbed by Palladium.	Total Hydrogen.
Min.	Volts.	Min.	c.c.	c.c.	c.c.	c.c.	Minutes.	Volts.	Min.	c.c.	c.c.	c.c.	c.c.
0	—0.633*	. . .	. . .	. . .	. . .	. . . .	0	—0.486*	. . .	. . .	. . .	. . .	. . .
8	—1.978	6.5	4.7	. . .	. . .	. .	0.5	—0.511	22	. . .	. . .	. .	. . .
11	—1 978	51	57	2.2	2.2	54.8	3.5	—0.494	32	0.02	. . .	. . .	. . .
21	—1.989	98	54.2	2.0	4.2	107.0	15	—0.463	48	0.3	. .	. . .	. . .
89	—1.993	145	56.2	1.8	6.0	161.4	18	—0.448	57	0.5	. . .	. . .	. . .
113	—1.993	194.5	55.2	1.8	7.8	214.8	21	—0.434	66	1.0	. . .	. . .	. . .
140	—1.994	229	53.2	2.0	9.8	266.0	24	—0.413	72	2.0	. . .	. . .	. . .
227	—1.986	275	54.6	2.0	11.8	318.6	31	—0.378	77	5.0	. . .	. . .	. . .
. . .	—0.743*	323	54.8	2.0	13.8	371.4	33.5	—0.378	107	16.6	0.8	0.8	15.8
231	—1.984	369	55.4	2.0	15.8	424.8	43	—0.297	166	22.9	0.6	1.4	38.1
. . .	—0.646*	412	52.4	2.0	17.8	475.2	67	—0.301	204	23.7	0.8	2.2	61.0
328	—2.000	459	55.3	2.0	19.8	528.5	75	—0.294	288	47.6	4.0	6.2	104.6
							87	—0.281	310	27.1	0.7	6.9	131.0
							96.5	—0.294	327	12.0	0.3	7.2	142.7
							104	—0.294	348.5	28.2	0.3	7.5	170.6
							113	—0.393†	373.0	31.3	0.8	8.3	201.0
							135	—0.223	406.7	47.0	0.5	8.8	247.5
							144	—0.223	440.3	36.0	0.4	9.2	283.1
							147	—0.364†	459	24.3	0.4	9.6	307
							154	—0.364	. . .	. . .	. . .	. . .	. . .

							171	—0.407					
							200	—0.251					
							208	—0.470†					
							226	—0.336					
							. . . . .	—0.494*					
							233	—0.383					
							244	—0.215‡					
							269	—0.294					
							. . . . .	—0.491*					
							277	—0.336					
							284	—0.166					
							297	—0.142					
							334	—0.166					
							360	—0.173					
							459	—0.486					

* No current passing through cell.
† Stirred solution in cathode chamber by removing accumulated hydrogen.
‡ Stirring did not reduce cathode discharge potential at this point as it had done earlier in the process.

NOTES: Date, July 24, 1907. The solution contained 1.000 gr. potassium nitrate (KNO_3), 1.000 gr. copper sulphate ($CuSO_4.5H_2O$), and 1.715 per cent. sulphuric acid (H_2SO_4) in 300 c.c. The cathode was of copper (the same piece of metal used in all the experiments where the gases evolved at anode and cathode were determined), 100 sq. cm. in area, and was fixed beneath an inverted cylindrical funnel with a glass stopcock at its point, so that the gas evolved might be collected and removed for analysis. Likewise, the anode, of platinum wire, 0.5 sq. cm. in area, was placed under an inverted burette, and the gas evolved collected and analyzed. The current was approximately 0.3 ampere throughout the experiment, and the temperature of the solution varied between 30° and 31° C. The anode solution was drawn up to the top of the burette at the beginning of the experiment, thus expelling all air. Similarly, the cathode chamber was filled with solution. The solution had been boiled previously to expel dissolved gases. The rate at which the anode gas was liberated was noted from the very beginning, and affords a check on the ammeter reading for the current passing, although the presence of some 4 per cent. of gas not absorbed by alkaline pyrogallol makes this less certain as a measure of the coulombs passed through the cell.

The gas evolved at the anode was transferred to a gas burette, measured, and immediately absorbed by alkaline pyrogallic acid solution in a gas pipette. With a current of 0.3 ampere, it was possible to complete the absorption of one portion of gas, about 50 c.c., before the next portion was ready for removal. The cathode gas was transferred from the cathode chamber to a gas pipette, and thence to the gas burette, where its volume was read. The gas was then passed through a palladium tube and the hydrogen absorbed. In each case, the palladium tube was regenerated, and the gas passed over it again to make sure that all the hydrogen had been absorbed. The capacity of the palladium tube for hydrogen was about 67 c.c. at 30° C. and 760 mm. pressure.

Anode and cathode discharge potential measurements also were made at the beginning, before the current was passed, and afterwards from time to time during the course of the electrolysis.

The passage of the current was twice interrupted—once

because owing to the severe heat, the work could not be continued, and again, because the faster evolution of hydrogen as the reduction neared completion rendered it impossible to complete the analyses of gas samples as fast as the gas was evolved. Since an important point in this experiment was to permit the least possible contamination of the gases by contact with water, it was thought advisable to sacrifice continuity of electrolysis to the securing of anode and cathode gas samples in the exact condition in which they were liberated. This is especially important; and besides, we have other reduction experiments giving continuous anode and cathode discharge potential-time curves, together with the yield of ammonia and of hydroxylamine.

Yield: After 229 minutes, 1 per cent. of the total nitrogen was present as hydroxylamine; 22.4 per cent. of the nitrogen as ammonia; 2.47 per cent. of nitrogen had been evolved at the cathode, and 6.9 per cent. of the nitrogen liberated at the anode. After 459 minutes, 50.5 per cent. of the nitrogen had been converted to ammonia; 0.9 per cent. was present as hydroxylamine; in all, 14 per cent. of the total nitrogen had been given off at the anode as nitrogen, and 6.8 per cent. of the total nitrogen evolved at the cathode as nitrogen. The temperature of the gases, as measured, was 31° C., and the pressure 764.2 mm.; deducting 33.4 mm. aqueous tension, gives 730.8 mm. actual pressure.[46]

The following formula was used for ascertaining the weight of the nitrogen:

$$W = 0.0000899 \times \text{volume of gas} \times \left(\frac{1}{1 + \alpha t}\right) \cdot \frac{P}{760} \cdot 14.04.$$

As to the utilization of current: 528.5 c.c. of oxygen gas, at 31° C. and 730.8 mm. actual partial pressure of the oxygen, is equivalent to 0.6559 gr. oxygen, which requires 7,932 coulombs for its liberation. A current of 0.3 ampere passed for 459 minutes, giving 8,262 coulombs. This leaves 330 coulombs wasted current at the anode.

At the cathode, 307 c.c. hydrogen, at 31° and 730.8 mm. actual partial pressure, was liberated, equivalent to 0.02382 gr., which requires 2,283 coulombs for its liberation. The reduction of

[46] The laboratory is very nearly at sea level.

50.5 per cent. of the total nitrogen in 1 gr. potassium nitrate to ammonia requires 3,856 coulombs, and the reduction of 0.9 per cent. to hydroxylamine, 52 coulombs. Altogether, this uses 6,191 coulombs, leaving 2,071 coulombs unaccounted for.

We have not sufficient analytical data on the composition of the nitrogenous gases given off at anode and at cathode to calculate the coulombs requisite for their liberation.

The low yield of ammonia in this experiment is, without doubt, due to the lack of free diffusion of the solution, caused by the presence of the gas-collecting tubes. The copper is stripped from the solution in the cathode chamber more rapidly than in the open beaker used in Section V. This increases the ratio of hydrogen to copper depositing, and the yield of ammonia drops, as it does at a copper cathode in sulphuric acid where no copper sulphate has been added to the solution. This effect is shown in the rise in the cathode polarization in Table XXXIV and in its drop after each stirring, which supplied more copper sulphate and more nitrate to the cathode.

Section VIII.

Reduction of Hydroxylamine at a Copper Cathode.

The statement of Tafel[47] that hydroxylamine is not reduced at a copper cathode in acid solution, and the very low yield of ammonia obtained by Flaschner[48] on electrolyzing hydroxylamine required confirmation. Using conditions very nearly the same as those recommended by Easton, hydroxylamine hydrochloride dissolved in 1.7 per cent. sulphuric acid was reduced at a copper cathode, and the yield of ammonia found to be very much higher than that indicated by Flaschner's work.

(R) Solution, 150 c.c., containing 0.3810 gr. hydroxylamine hydrochloride ($NH_2OH.HCl$) and 1.7 per cent. sulphuric acid (H_2SO_4); cathode, smooth, recently deposited copper, 100 sq. cm. in area; anode, polished platinum, 0.5 sq. cm. in area; current, 1 ampere; time, 348 minutes; temperature, 31° C. Yield: Per cent. of total nitrogen as ammonia, 58.8; as hydroxylamine, 0.5. Anode and cathode discharge potentials are given below in Table XXXV.

[47] l. c.
[48] l. c.

TABLE XXXV.

Discharge potential at copper cathode and platinum anode during the reduction of hydroxylamine in acid solution.

Anode.		Cathode.	
Minutes.	Volts.	Minutes.	Volts.
0	—0.630*	0*	—0.509†
0	—0.800*	0*	—0.441‡
5	—1.410	9	+0.033‖
21	—1.410	17	+0.028
82	—1.410	38	+0.065
125	—1.637	80	+0.065
...	.....	127	+0.376
...	.....	.....	.....
...	.....	348	.....

* No current on.
† No H_2SO_4 added.
‡ H_2SO_4 added.
‖ Current passing.

The quantity of hydroxylamine hydrochloride taken, 0.3810 gr., requires 0.016572 gram hydrogen for complete reduction to ammonia, which is equivalent to 1,588 coulombs. The total coulombs passed in experiment (R) was 20,880. Since the yield of ammonia was 58.8 of the theoretical, the quantity of electricity actually used in converting hydroxylamine to ammonia is less, *i. e.,* 934 coulombs. This gives as the current efficiency, in the reduction of hydroxylamine to ammonia, 4.46 per cent.

To determine the effect of copper deposition upon the reduction of hydroxylamine, as well as to confirm this unexpected high yield of ammonia, experiments (S) and (T) were made, using respectively 1 gr. and 5 gr. of $CuSO_4.5H_2O$ in solution, the other conditions being very nearly the same.

(S) Solution, 150 c.c., containing 0.3810 gr. hydroxylamine hydrochloride ($NH_2OH.HCl$), 1.000 gr. copper sulphate ($CuSO_4.5H_2O$), and 1.7 per cent. sulphuric acid (H_2SO_4); cathode, the same piece of copper used in experiment (R), 100 sq. cm. in area; anode, the same as in experiment (R), polished platinum, 0.5 sq. cm. in area; current, 1 ampere; time, 180 minutes; temperature, 30° C. Yield: Per cent. of total nitrogen as ammonia, 65.3; as hydroxylamine, 2.3. Anode and cathode discharge potentials are given in Table XXXVI.

TABLE XXXVI.

Discharge potential at copper cathode and platinum anode during the reduction of hydroxylamine in acid solution with copper sulphate present.

Anode.		Cathode.	
Minutes.	Volts.	Minutes.	Volts.
0	—0.608*	0	—0.483*
1	—1.505	4	—0.217
3	—1.790	15	—0.032
20	—1.540	22	—0.061
37	—1.398	34	—0.032
58	—1.385	39	—0.032
76	—1.398	44	—0.033
99	—1.564	81	—0.055
162	—1.726	95	—0.055
....	.....	171	—0.063
....	.....	....	.....
180	.....	180	.....

* No current passing.

The cathode discharge potential here in experiment (S) is much lower than in Table XXXV, experiment (R), as might be expected with copper continually depositing. The anode discharge varies considerably, and finally reaches a higher value than that given in experiment (R); this is not surprising, as the interaction of chlorine, oxygen, sulphate, nitrate, nitrites and hydroxylamine is involved. The deposition of copper during the reduction has increased the yield of ammonia from 58.8 to 65.3 per cent. of the total nitrogen.

The quantity of electricity required to deposit the copper from 0.5 gr. copper sulphate ($CuSO_4.5H_2O$) is 387 coulombs. Deducting this from 10,800 coulombs, the total quantity passed, gives 10,413 coulombs available for the reduction of hydroxylamine. The conversion of 65 per cent. of the total nitrogen to ammonia takes 1,008 coulombs, consequently, the current efficiency is 9.7 per cent.

(T) Solution, 150 c.c., containing 0.3810 gr. hydroxylamine hydrochloride ($NH_2OH.HCl$), 5.000 gr. copper sulphate ($CuSO_4.5H_2O$), and 1.7 per cent. sulphuric acid (H_2SO_4); cathode, copper, 100 sq. cm. in area; anode, polished platinum,

20 sq. cm. in area; current, 1 ampere; time, 180 minutes; temperature, 26° C. Yield: Per cent. of total nitrogen as ammonia, 65.8; as hydroxylamine, 0.03. All the copper was deposited from solution. Anode and cathode discharge potentials are given in Table XXXVII.

TABLE XXXVII.

Discharge potential at copper cathode and platinum anode during the reduction of hydroxylamine in acid solution with copper sulphate present.

Anode.		Cathode.	
Minutes.	Volts.	Minutes.	Volts.
0	—0.607*†	26	—0.362
0	—0.579*‡	33	—0.300
5.5	—1.979‖	35	—0.300
38	—2.115	43	—0.279
82	—2.004	53	—0.209
112	—1.947	66.5	—0.146
174	—1.946	77	—0.093
		84	—0.083
Cathode.		97	—0.066
		108	—0.055
0	—0.551*†	122	—0.055§
0	—0.503*‡	158	—0.055
1	—0.488‖	176	+0.008
6	—0.470	177	+0.008
9	—0.411	178.5	+0.008
13	—0.404	179.5	—0.013
15.5	—0.390	.....	.....
17	—0.390	.....	.....
21	—0.376	.....	.....

* No current passing.
† Hydroxylamine and copper sulphate alone, no sulphuric acid added as yet.
‡ Sulphuric acid added.
‖ Current passing.
§ Copper all deposited.

To deposit the copper from 5.000 gr. copper sulphate ($CuSO_4.5H_2O$) requires 3,867 coulombs; 10,800 coulombs were passed; this leaves 6,933 coulombs available for the reduction of hydroxylamine. The yield of ammonia was 65.8 per cent. of the total nitrogen, therefore that per cent. of 1,588 coulombs (needed for reducing 0.3810 gr. $NH_2OH.HCl$), or 1,032 coulombs were actually used. This gives a current efficiency of 14.9 per cent. in the conversion of hydroxylamine to ammonia.

It is established, then, that hydroxylamine is reduced at a copper cathode, and that the deposition of copper during the reduction has a marked influence in increasing the yield. It seems very probable that the nitrogen lost from the solution is liberated in some gaseous form at either anode or cathode, probably at both. The reduction of nitrate at a copper cathode need not proceed directly to ammonia, but may go through the hydroxylamine stage.

Section IX.

Reduction of Nitrite at a Copper Cathode.

Two experiments were made to ascertain the completeness with which a nitrite is reduced to ammonia at a copper cathode.

(U) Solution, 150 c.c., containing[49] 0.3724 gr. sodium nitrite ($NaNO_2$) and 1.7 per cent. sulphuric acid (H_2SO_4); cathode, smooth copper, 100 sq. cm. in area; anode, polished platinum, 0.5 sq. cm. in area; current, 1 ampere; time, 126 minutes; temperature, 30° C. Yield: Per cent. of total nitrogen as ammonia, 59 per cent.; left in a form oxidized by permanganate, 0.1 per cent., reckoned as hydroxylamine; 0.2 c.c., 0.01 N potassium permanganate ($KMnO_4$) required for the whole 150 c.c. of solution. Anode and cathode discharge potentials are given in Table XXXVIII.

[49] Exactly determined by titration with permanganate, according to Kinnicut and Nef.; Sutton, Volumetric Analysis, p. 273.

Table XXXVIII.

Discharge potential at platinum anode and copper cathode during the reduction of nitrate in acid solution.

Anode.		Cathode.	
Minutes.	Volts.	Minutes.	Volts.
0	—0.798*†	0	—0.360*†
0	—1.046*‡	0	—0.522*‡
0	—1.046*‖	0	—0.508*‖
1	—1.549§	8	—0.296§
3	—1.713	18	—0.275
21	—1.946	26	—0.211
71	—1.934	38	—0.204
...	.....	67	—0.161
...	.....	125	—0.148

* No current passing.
† No H_2SO_4 present.
‡ + 0.790 gr. H_2SO_4.
‖ + 2.372 gr. H_2SO_4.
§ Current passing.

In view of the fact that the cathode potential remains low throughout this reduction, the existence of practically no oxidizable bodies (by permanganate) at the end of 126 minutes of electrolysis is interesting. The anode discharge in this nitrate reduction, too, is much higher[50] than in the nitrate solution, indicating a breaking up of the nitrate; nitrous fumes were easily detected at the anode by their odor. The anode discharge potential in hydroxylamine reduction is likewise high. These reactions at the anode require further study, involving collection and analysis of gaseous products. As to the current efficiency: 0.3724 gr. sodium nitrite ($NaNO_2$) required 0.03260 gr. hydrogen for complete reduction to ammonia, which corresponds to 3,148 coulombs; since 59 per cent. of the sodium nitrite ($NaNO_2$) was reduced to ammonia, the actual quantity of electricity used in this process is 1,857 coulombs. During the electrolysis, 7,560 coulombs passed through the cell, therefore the current efficiency is 24.5 per cent.

In the following experiment, copper sulphate was added to the solution, to see if it gave an increased yield of ammonia in

[50] By higher is meant nearer to the chosen zero, going up from negative to positive.

the reduction of nitrite, as is the case with nitrate and with hydroxylamine.

(V) Solution, 150 c.c., containing 0.3724 gr. sodium nitrite ($NaNO_2$), 0.750 gr. copper sulphate ($CuSO_4.5H_2O$), and 1.7 per cent. sulphuric acid (H_2SO_4); cathode, copper, 100 sq. cm. in area; anode, polished platinum, 0.5 sq. cm. in area; current, 1 ampere; time, 255 minutes; temperature, 30° C. Yield: Per cent. of total nitrogen as ammonia, 61.4; as bodies capable of oxidation, 0.4 c.c. 0.1 N permanganate required for the whole 150 c.c. of solution, equivalent to 0.2 per cent. hydroxylamine. Anode and cathode discharges are given in Table XXXIX.

TABLE XXXIX.

Discharge potential at platinum anode and copper cathode during the reduction of nitrite in acid solution with copper sulphate present.

Anode.		Cathode.	
Minutes.	Volts.	Minutes.	Volts.
0	—0.808*†	0	—0.517*†
0	—0.829*‡	0	—0.496*‡
3	—1.512‖	1	—0.510‖
5	—1.582	2	—0.503
17	—1.859	7	—0.489
35	—1.902	14	—0.433
52	—1.929	18	—0.433
143	—1.963	33	—0.384
....	....	56	—0.220
....	....	60	—0.170
....	....	74	—0.150
....	....	140	—0.121

* No current passing.
† No H_2SO_4 added.
‡ H_2SO_4 added.
‖ Current passing.

The copper depositing from solution has a marked effect upon the cathode potential, which is below —0.490 volt during the first 7 minutes of electrolysis, and after 33 minutes still is at —0.384 volt. With no copper sulphate added, the cathode potential at the end of 26 minutes was —0.211 volt. One expects this effect to appear in the yield of ammonia as well, but the increase observed is only from 59 per cent. to 61.4 per

cent., some 2.4 points. In this last experiment, (V), too, the material capable of oxidation remaining in solution at the end of the run is negligible, and doubtless due to the oxidation of ammonia at the anode. This fact again points to the loss of nitrogen in gaseous forms at anode and cathode, which is likewise strongly suggested by the fairly regular drop in the anode polarization as electrolysis proceeds (see Table XXXIX), and it seems altogether likely that this increased yield of ammonia in the presence of copper sulphate is really due to the copper depositing from solution, and not to the longer period of electrolysis in the experiment. The oxidation and nitrogen loss at the anode, too, extends over a longer time here, and tends to lower the yield of ammonia.

Current efficiency: The quantity of copper sulphate ($CuSO_4.5H_2O$) used, 0.750 gr., requires 5,800 coulombs for its deposition, and as 15,300 coulombs passed through the cell, there were left 9,500 coulombs available for the reduction of nitrite. The yield of ammonia being 61.4 per cent., the quantity of electricity actually used in its formation is 1,933 coulombs, which divided by 9,500, gives 20.2 per cent. as the current efficiency. Or, if the total quantity of electricity passed be considered, rather than that left over by the copper deposition, the current efficiency is lower, *i. e.,* 12.6 per cent.

From the foregoing experiments, (U) and (V), it is clear that if a nitrate be converted to nitrite at a copper cathode in sulphuric acid solution, either in presence or absence of copper sulphate, reduction to ammonia takes place until practically all nitrite or lower oxides of nitrogen are reduced to ammonia, or leave the solution in gaseous form at anode or cathode.

Section X.

Discharge at Anode.

LeBlanc[51] gives as the decomposition voltage between platinum points, *i. e.,* at high current density, such as obtained at the anode in this series of experiments, the following values: Nitric acid, 1.69 volts; sulphuric acid, 1.67 volts; hydrochloric acid, 1.69 volts; potassium hydroxide, 1.67 volts; sodium hydroxide,

[51] Zeit. phys. Chem., 8, 299 (1891).

1.69 volts. Taking Ostwald's value for the single potential of hydrogen as —0.277 volt, this leaves an anode polarization of 1.393 volts due to oxygen where the decomposition point is 1.67 volts, and of 1.413 volts where the decomposition point is 1.69 volts.

1. Hydroxylamine. The anode polarization for hydroxylamine hydrochloride in sulphuric acid, given in Table XXXV,

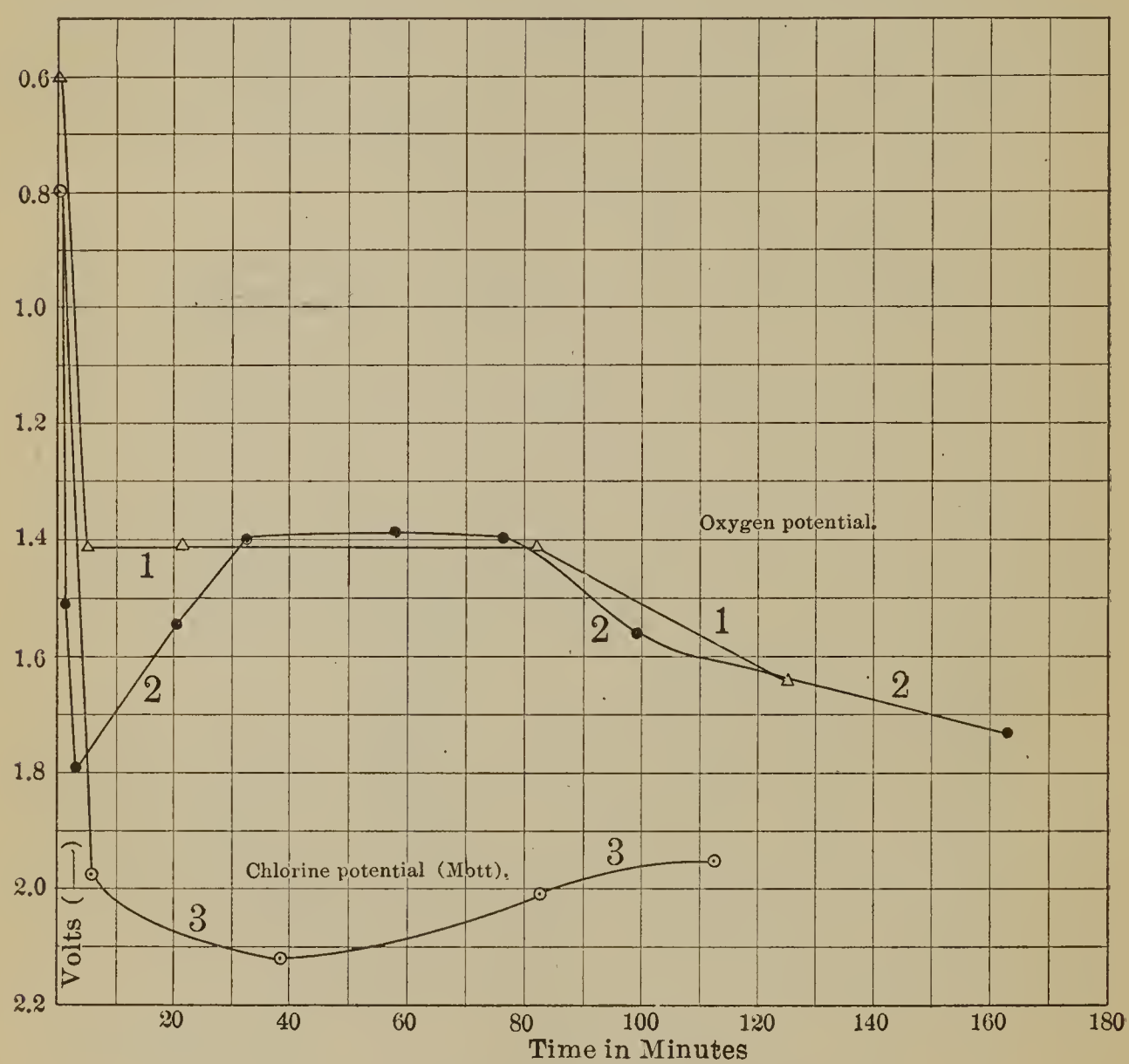

FIGURE 7. Discharge potential at platinum anode.

Curve 1 = △ = $NH_2OH . HCl + H_2SO_4$—Table XXXV.
Curve 2 = ● = $NH_2OH . HCl$ + 1 gram $CuSO_4 . 5H_2O + H_2SO_4$—Table XXXVI.
Curve 3 = ⊙ = $NH_2OH . HCl$ + 5 grams $CuSO_4 . 5H_2O + H_2SO_4$—Table XXXVII.

drops rapidly to 1.410 volts, and remains at this oxygen value for 82 minutes, when it gradually falls to —1.635 volts, after 125 minutes of electrolysis. (See Curve 1, Fig. 7.)

When copper sulphate was added (1.000 gr. $CuSO_4.5H_2O$) to the solution containing hydroxylamine hydrochloride and

sulphuric acid, the anode polarization dropped within three minutes to —1.79 volts, as might be expected with chlorine in the solution. Mott[52] gives a discharge potential of —1.81 volts for chlorine and oxygen liberated together at a platinum anode. As shown by Curve 2, Fig. 7, this polarization rises gradually, until, after 36 minutes of electrolysis, a value of some 1.4 volts is reached, and this persists 40 minutes longer, and then falls to —1.73 volts at the end of the run, 162 minutes. (See Table XXXVI.)

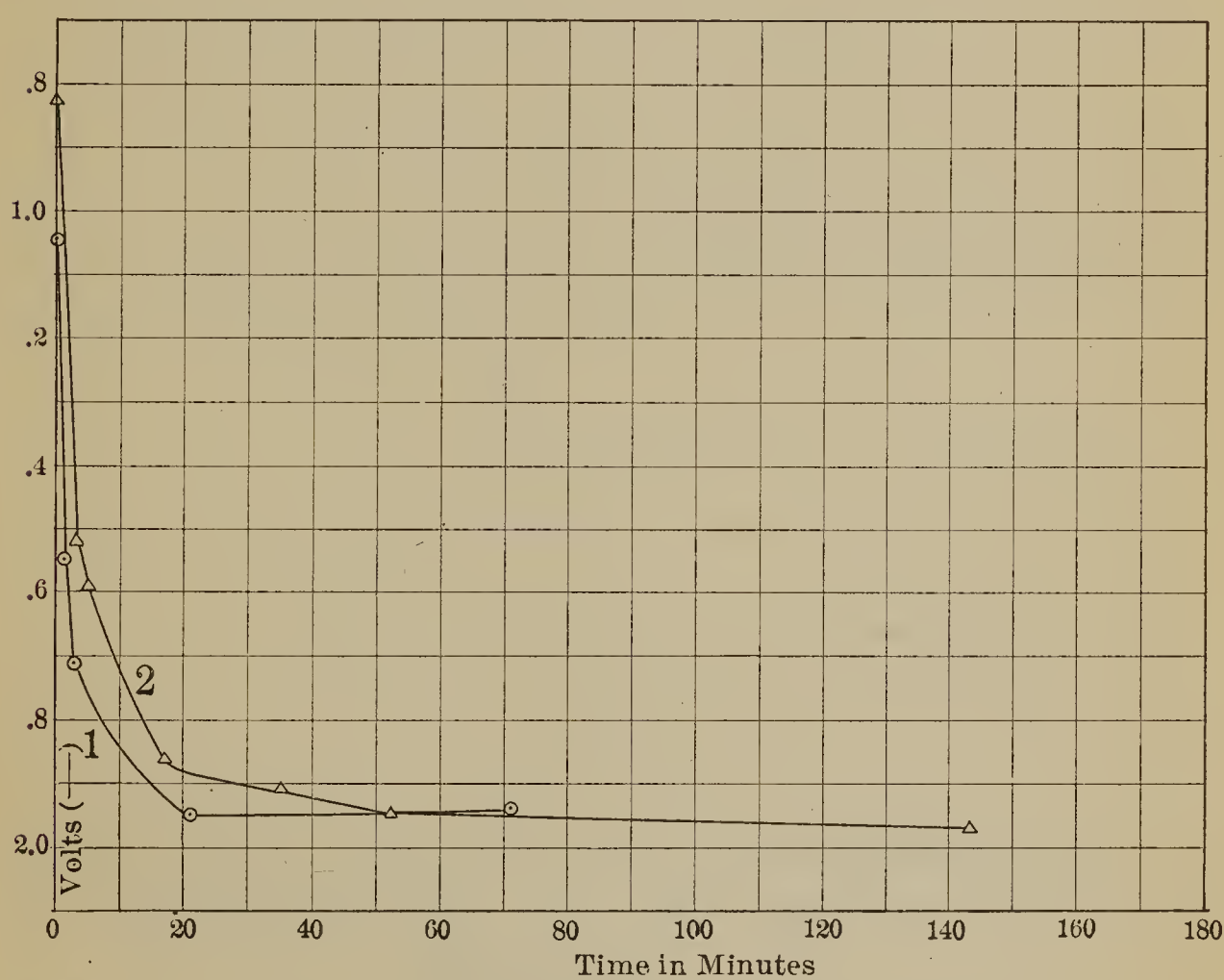

FIGURE 8. Discharge potential at platinum anode.
Curve 1 = ⊙ = $NaNO_2 + H_2SO_4$—Table XXXVIII.
Curve 2 = △ = $NaNO_2 + H_2SO_4 + CuSO_4$—Table XXXIX.

With 5.000 gr. copper sulphate ($CuSO_4.5H_2O$) in this same solution, the anode discharge drops within 6 minutes to —1.975 volts, and remains below —2.000 volts during the next 76 minutes, when it gradually rises to a permanent value of —1.95 volts. At no time in this run was the oxygen potential reached, as in the experiments in Tables XXXV and XXXVI. This low anode discharge suggests that an oxidation is taking place.

[52] Trans. Am. Electrochem. Soc., **5**, 79 (1904).

2. Nitrite. Curve 1, Fig. 8, shows the anode discharge in sodium nitrite solution acidified with sulphuric acid. The polarization falls rapidly, and soon reaches a permanent value of —1.95 volts, which is the same as that for the hydroxylamine solution. When copper sulphate is added, the anode discharge is higher; at 6 minutes it is —1.58 volts, and at 17 minutes still remains 0.1 volt above the polarization value, —1.95 volts, which it finally reaches after some 75 minutes of electrolysis. The

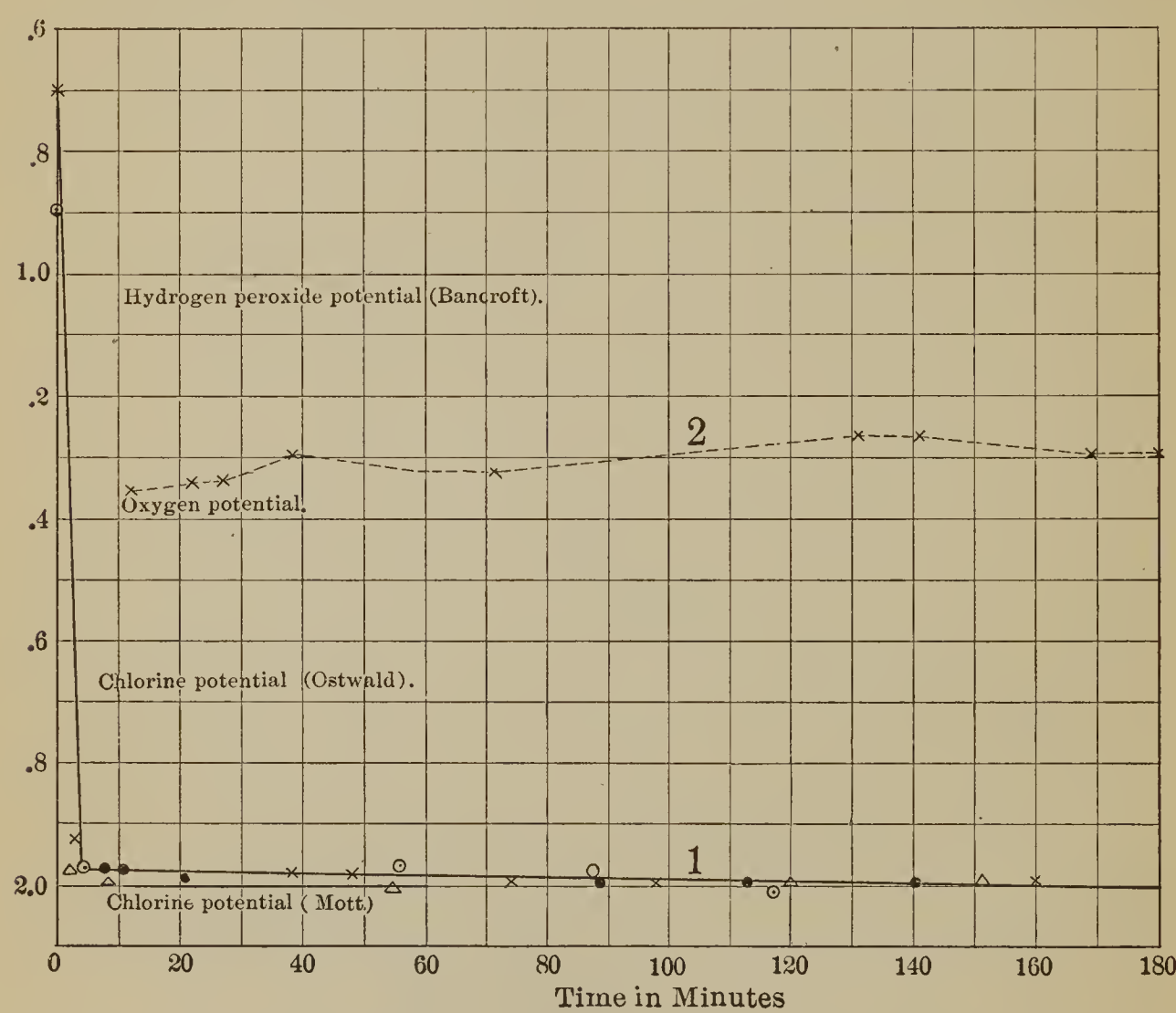

FIGURE 9. Discharge potential at platinum anode, current density 200 amperes per sq. dm.

Curve 1. $KNO_3 + CuSO_4 + H_2SO_4$.
⊙ = Table XXXI; × = Table XXXII;
△ = Table XXXIII; ● = Table XXXIV.
Curve 2. $KNO_3 + KOH$—Table XXIX.

conversion of nitrite to nitrate at the anode, and the ultimate presence of ammonia, hydroxylamine and nitrate at the anode in this solution leads one to expect that the anode polarization will be nearly the same in nitrite and in nitrate solutions.

3. Nitrate. The curve in Fig. 9 shows a typical anode

discharge in a solution of potassium nitrate acidulated with sulphuric acid, and containing copper sulphate. The points marked by a circle ⊙ are plotted from data in Table XXXI; those marked by a cross, ×, from Table XXXII; those marked by a triangle, △, from Table XXXIII; and those marked by a dot, . , from Table XXXIV. For all of these points it was found that nitrogen in gaseous form was liberated at the anode. The polarization value, about —1.98 volts, maintained in the electrolysis of these nitrate solutions, is practically the same as that shown by the nitrite solutions in Fig. 8. The anode discharges given in the other tables are in good accord with these values, and need not be plotted.

Anode discharge in alkaline solution. In Table XXVI, Section VI, is given the discharge potential from a polished platinum anode in an alkaline solution of potassium nitrate. This is shown in Fig. 9 by a dotted curve, 2. It lies higher than the same discharge in acid solution.

CONCLUSIONS.

From the data presented in the foregoing pages, the following conclusions are justified:

1. Using a copper cathode and a porous diaphragm in dilute sulphuric acid, increase in concentration of the acid increases the yield of ammonia and decreases the yield of hydroxylamine.

2. The increase of current density decreases the yield of ammonia when a copper cathode is used, but increases the yield of ammonia when a platinum cathode is used.

3. The effect of temperature upon the yield of either ammonia or hydroxylamine through the range ordinarily obtained is so slight as to render rigid temperature control unnecessary.

4. The yield of ammonia is greatly increased by the continued deposition of copper at the cathode, and the suggestion made by Tafel, that this effect is due to a catalytic action of the deposited spongy copper, is questionable, since the same effect is produced when copper is continually deposited upon the amalgamated copper cathode, whose surface remains smooth throughout the reduction. This effect reaches a maximum; thus, when nitric acid is reduced at a copper cathode in a solution highly con-

centrated with respect to copper sulphate, the yield of ammonia is less than at a lower concentration. This result was also observed by Ingham.

5. In general, a low cathode discharge accompanies a high yield of ammonia when the current density is the same.

6. Nitrogen, either as free nitrogen or in the form of oxides, is given off at both copper cathode and a platinum anode.

7. It is probable that the reduction of nitric acid to ammonia at a copper cathode involves the formation of hydroxylamine as an intermediate stage.

8. The electrolysis of sodium nitrite at a copper cathode in sulphuric acid solution reduces all of the nitrogen to a form which is not oxidized by potassium permanganate.

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A paper read by title at the Twelfth General Meeting of the American Electrochemical Society, in New York City, October 19, 1907, President C. F. Burgess in the chair.

A FURTHER CONTRIBUTION TO THE STUDY OF CONCENTRATION CELLS.

By Henry S. Carhart and F. J. Mellencamp.

In a paper by one of the present writers, in Vol. X of the Transactions of this Society, the proposition was maintained that "whenever the conditions are such that the heat of reaction and of dilution is negligible, the first term (of the Helmholtz equation) becomes zero, and only the second, T dE/dT, remains." The conditions referred to in this statement restrict the solutions to very dilute ones; otherwise the heat of dilution is not negligible.

The present paper, which is to be regarded as preliminary only, presents a comparison between the observed and computed values of the E. M. F. of several concentration cells made up with solutions of any concentrations for which the heats of dilution have been determined. The work is still in progress and it is hoped that many more examples may be added.

Whenever the heats of dilution (reckoned from any standard concentration) of the two solutions in the two legs of the cell differ, this difference is available as energy to produce an E. M. F. represented by the first term of the Helmholtz equation. If then the temperature coefficient of the cell is positive, the E. M. F., due to a positive resultant heat of dilution, is to be added to the value of T dE/dT.

The electrode in the more dilute solution of a concentration cell is the anode. Now when the heat of dilution increases with the dilution, that is, when dilution generates heat, then more heat is generated when a gramme-equivalent of the electrode goes into solution at the anode than is absorbed by the removal of a gramme-equivalent of the same metal at the cathode. Let us suppose the quantities of the two solutions so great that the entrance of a gramme-equivalent of the metal at the anode and the

removal of an equal quantity from the solution about the cathode do not change the concentrations of the solutions. Then at the anode the gramme-equivalent of the metal becomes a salt, which goes into solution and is diluted down to the same concentration as that of the solution about the anode; at the same time a gramme-equivalent of the same metal is removed from the more concentrated solution surrounding the cathode, and this latter operation absorbs less energy than is derived from the former when the heat of dilution is positive. This surplus of energy is available as free energy to produce E. M. F. and to transport electricity across the cell from the more dilute to the more concentrated solution.

According to Thomsen, for one gramme-molecule, $ZnSO_4.20H_2O$ diluted to $ZnSO_4.50H_2O$ generates 318 calories of heat. Also, $ZnSO_4.20H_2O$ diluted to $ZnSO_4.400H_2O$ generates 400 calories of heat. Hence, $ZnSO_4.50H_2O$ — $ZnSO_4.400H_2O$ is equivalent to 82 calories. This is all free energy and gives rise to

$$\frac{82 \times 4.186}{2 \times 96{,}550} = 0.00178 \text{ volt E. M. F.}$$

The temperature coefficient of a cell set up with electrodes of zinc amalgam in the above solutions is positive and equal to 0.0000528 as a mean of a number of measurements differing but little among themselves. Hence for 25° the term T dE/dT is $298 \times 0.0000528 = 0.01573$. Then $E = 0.00178 + 0.01573 = 0.0175$ volt as the computed E. M. F. of this cell at 25°. The observed E. M. F. was 0.0171 volt.

In the table following E_h is the E. M. F., due to the heat of dilution and $T\frac{dE}{dT}$ is the E. M. F. derived from the heat of the surroundings.

Solutions.	$\frac{dE}{dT}$	$T\frac{dE}{dT}$	E_h	Comp. E.M.F.	Obs. E.M.F.
$ZnSO_4 . 50 H_2O$ $ZnSO_4 . 400H_2O$	0.0000528	0.01573–25°	0.00178	0.0175	0.0171
$ZnSO_4 . 100H_2O$ $ZnSO_4 . 400H_2O$	0.000032	0.00954–25°	0.00072	0.0103	0.0101
$ZnSO_4 . 50 H_2O$ $ZnSO_4 . 100H_2O$	0.0000174	0.00507–25°	0.00106	0.0061	0.0062
$ZnSO_4 . 50 H_2O$ $ZnSO_4 . 200H_2O$	0.0000344	0.01025–25°	0.00145	0.0117	0.0116
$CdSO_4 . 50 H_2O$ $CdSO_4 . 400H_2O$	0.0000188	0.00557–23°	0.01080	0.0164	0.0164
$CdSO_4 . 50H_2O$ $CdSO_4 . 200H_2O$	0.000009	0.00246–0°	0.00847	0.0109	0.0108
$CdSO_4 . 100H_2O$ $CdSO_4 . 400H_2O$	0.0000155	0.00423–0°	0.00604	0.0103	0.0099
$CuSO_4 . 60H_2O$ $CuSO_4 . 200H_2O$	0.0000248	0.00739–25°	0.00251	0.0099	0.0098
$ZnCl_2 . 21.9H_2O$ $ZnCl_2 . 386H_2O$	—0.000104	—0.02839–0°	0.10100	0.0726	0.0751

The last case furnishes a specially instructive illustration of the correctness of the principle involved, because the temperature coefficient is negative, as in most voltaic cells. The E. M. F. of this cell is accordingly less than the value derived from the heat of dilution. The concentrations of the solutions of zinc chloride were determined by titration, and the corresponding heats of dilution were obtained by interpolation by means of a smooth curve.

The electrodes in every case were amalgams not containing enough of the metal to be in the solid state at any temperature employed in finding the temperature coefficient. A change of phase of the amalgam from solid to liquid made a break in the value of the coefficient at the point of change.

The electrodes were composed of a glass cup with a glass tube sealed into the bottom on the inside, and extending up out of the bath. The cup was partly filled with the amalgam; the tube also was filled and the amalgam in the cup was put into connection with that in the tube by means of a short platinum wire sealed through the glass in the cup. The two legs of the cell were not in communication except at the time of making an observation. At other times the glass stop-cock in the connecting tube was closed. After the cell was set up it was always allowed to stand until equilibrium had been reached before taking and recording an observation.

The electromotive forces were measured by means of a Wolff's potentiometer in comparison with a standard cell.

Physical Laboratory,
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A paper read at the Twelfth General Meeting of the American Electrochemical Society, in New York City, October 19, 1907, President C. F. Burgess in the chair.

THE ELECTROLYTIC THEORY OF THE CORROSION OF IRON.

By Allerton S. Cushman.

The work that I am going to speak about has been presented also to the American Society for Testing Materials, and has been published in a bulletin of the Department of Agriculture.[1] As I have no new contribution to make to-day, I shall attempt to be as brief as possible in putting the subject before you.

In considering the corrosion of iron it is important to remember that iron is a metal which readily combines with or dissolves nearly all the other elements. With possibly one or two exceptions, there are no elements that do not either dissolve in or combine readily with iron. It is also unique in the fact that very small quantities of impurities suffice to entirely change its physical characteristics. On account of this fact metallurgists scrutinize the hundredth of a per cent. of some of the principal impurities that are generally associated with this metal. This is particularly true, for instance, of the element phosphorus. It is so important to modern metallurgy that the amount of phosphorus should be controlled in certain forms of steel that an animated discussion is going on at the present time between certain interests as to the control of the amount of phosphorus that steel shall carry, and the question at issue amounts to no more than a few hundredths of one per cent.

Manganese is also an element which is nearly always associated in modern metallurgy with iron and steel. Manganese decreases the electrical conductivity of iron, and as the percentage of manganese, starting from zero, rises, the electrical resistance increases up to a certain specific maximum. You will see that if the presence of manganese in iron raises the electrical resistance, any change in the distribution of the manganese means that there will not be a constant electrical conductivity throughout its mass,

[1] Bulletin No. 30, Office of Public Roads, Dept. of Agriculture.

or on any given surface. One who is familiar with the methods of modern metallurgy knows that the manganese is added for certain specific purposes, not as a rule quantitatively, but in accordance with the views of the iron master who has control of the mill or furnace. Moreover, the manganese is usually added by throwing lumps of ferro-manganese into the molten metal, either in the furnace itself, or in the ladle into which it has been poured. Chemists know the extreme care that has to be taken in order to get uniform mixtures of substances in the course of chemical operations. In the large scale of metallurgical processes, even if it were possible to take great care in the mixing, it still happens that when iron is cooled from the molten state, segregation takes place; that is to say, the impurities, although they may have been thoroughly mixed in the molten mass, do not remain homogeneously distributed after the metal is cooled.

For these reasons we must remember that in studying iron and steel from the standpoint of their stability, under the conditions of service, we are not dealing with homogeneous pure metal. It is not difficult for an electrochemist to believe that when such material is immersed in, or even brought into contact with, an electrolyte, electrolysis will take place upon the surface, and thereby induce rapid corrosion. It is probable that the corrosion of all metals is more or less due to electrochemical action. Before metals can be attacked at ordinary temperatures in the presence of water they must first pass into solution, and in passing into solution become ionized. This is true of copper, zinc, lead and the other metals that suffer corrosion.

In accordance with the conceptions of Nernst and the modern theory of solutions, all metals have a certain solution pressure which will operate until counterbalanced by the osmotic pressure. Iron, however, appears to differ from the other metals in one important respect. The corrosion of iron does not take place evenly and uniformly over the surface. On the contrary, it is a matter of common observation that iron corrodes rapidly at certain weak points, the effect produced being known as pitting. That this effect is produced by local electrolysis would hardly be doubted, even if it were not possible to demonstrate it by the use of the ferroxyl indicator.

Early in this investigation the writer observed that whenever a specimen of iron or steel is immersed in water or a dilute neutral solution of an electrolyte to which a few drops of phenolphthalein indicator has been added, a pink color is developed. If the solution is allowed to stand perfectly quiet, it will be noticed that the pink color is confined to certain spots or nodes on the surface. The pink color of the indicator is a proof of the presence of hydroxyl ions and thus indicates the negative poles.

Since phenolphthalein shows only the nodes where solution of iron and subsequent oxidation can not take place, Dr. W. H. Walker suggested the addition of a trace of potassium ferricyanide to the reacting solution, in order to furnish an indicator for the ferrous ions whose appearance marks the positive poles. If iron goes into solution, ferrous ions must appear, which, with ferricyanide, form the well-known Turnbull's blue compound. Going a step farther, Walker suggested stiffening the reagent with gelatin or agar-agar, so as to prevent diffusion and preserve the effects produced. For this combined reagent, which indicates at one and the same time the appearance of hydroxyl and ferrous ions at opposite poles, the writer has suggested for the sake of brevity the name "ferroxyl." If the reagent has been properly prepared the color effects are strong and beautiful. In the course of a few days the maximum degree of beauty in the colors is obtained, after which a gradual deterioration sets in.

In the pink zones, as would naturally be expected, the iron remains quite bright as long as the pink color persists. In the blue zones the iron passes into solution and continually oxidizes, with a resulting formation of rust. Even the purest iron develops the nodes in the ferroxyl indicator, but impure and badly segregated metal develops the colors with greater rapidity and with bolder outlines. This result would of course be expected, as in pure iron the formation of poles would be conditioned by a much more delicate equilibrium than in impure iron, where changes in concentration of the dissolved impurities would stimulate the electrolytic effects.

In the writer's opinion these effects which are produced in the ferroxyl indicator constitute a visible demonstration of electrolytic action taking place on the surface of iron, and causing rapid corrosion at the positive nodes. We have, however, still

another ocular demonstration of the truth of this theory. If a section of rolled metal, such as sheet or plate, is immersed in water, if the electrolytic theory is correct, rusting must take place with the establishment of positive and negative spots or areas. At the positive points iron will pass into solution and be rapidly oxidized to the loose colloidal form of ferric hydroxide which is characteristic of rust formed under these conditions. It is a well-known fact that colloidal ferric hydroxide will move or migrate to the negative pole if subjected to electrolysis. We may therefore consider the possibility of two separate effects that may be produced, viz., when a positive center is surrounded by a negative area, and vice versa. These two conditions may be graphically represented by the two circles A and B: $- \begin{smallmatrix} - \\ + \\ - \end{smallmatrix} - + \begin{smallmatrix} + \\ - \\ + \end{smallmatrix} +$.

Now, as rusting proceeds we should expect in the case of A that the ferric hydroxide would be piled up in a cone at the center. That this is precisely what is taking place whenever a sheet of metal rusts under water, a low-power microscope very clearly shows.

The photomicrographs, in which the craters and cones are clearly shown, have been published in the bulletin referred to above.

If you are willing to accept the electrolytic theory of corrosion you will very naturally inquire in what respect it points the way to an improvement in the conditions as they exist at the present time. It follows from what has been said that the more carefully lack of homogeneity and bad segregation are guarded against during the processes of manufacture, the less likely is the metal to suffer from rapid corrosion. If the iron contains metallic impurities dissolved in it such as manganese, which differ electrochemically from iron, trouble is sure to ensue if there is a lack of homogeneity in the distribution of the impurity. In the old days, when iron was made more slowly and received more careful working than is possible in the present day, serious corrosion of iron was not the important problem it has since become.

The writer has in his possession a hand-forged nail which is still in good condition, which was driven in the old Masonic Hall at Richmond, Virginia, in 1807, and for a long portion of this time it has been freely exposed to the weather. There is a widespread opinion, which the writer shares, that the old re-wrought

or puddled iron of thirty years ago is more resistant to corrosion than most of the modern steels.

But the interesting point is that modern steels vary so widely from each other. If we have a metal in which the electrical potential for any reason varies from point to point on the surface we have the precise conditions which are necessary in order to establish the local nodes of electrolytic action on the surface which lead to rapid corrosion. It is apparent, therefore, that if we are to allow the presence in structural steel of comparatively high percentages of metallic impurities, such as manganese, we must attempt to obtain an extremely homogeneous distribution of such impurities. It is for this reason principally, in the opinion of the writer, that the more quickly and more carelessly the metal is manufactured and rolled, the more quickly it disintegrates under corrosive influences. As has been pointed out before, there are two methods of meeting the problem: first, to keep the percentage of metallic impurities as low as possible, and secondly, to guard against segregation and imperfect chemical homogeneity in the metal. In experiments we have made looking to the manufacture of a corrugated steel culvert for use in road building, it has been found by the author that corrugated metal, running as low as 0.04 manganese, has been more resistant to the corrosive test employed than the ordinary steel of the day, which usually carries about 0.5 per cent. manganese. Material of this kind has not been available for a sufficient length of time to determine whether under service conditions this low manganese metal will be longer lived, but it can safely be stated that the indications are all in its favor.

Considerable attention has been given to the peculiar passive condition that can be induced on the surface of iron by contact with solutions of certain oxidizing agents. Without going into the details of this phenomenon, which have been already published, I will refer briefly to the peculiar action of chromic acid and its salts. Polished specimens of steel may be kept indefinitely without suffering corrosion when immersed in a dilute solution of potassium bichromate. On first thought it would seem a paradox that a strong oxidizing agent should have the effect of preventing the oxidation of iron, and yet this is the case.

According to the theory of the writer, the oxidizing agent

polarizes the surface of the iron to the condition of an oxygen electrode, so that it is immune from the attack of the hydrogen ions; thus the whole electrolytic process is checked or inhibited. A curious feature of this action is, that it is to a certain degree persistent after the metal has been removed from contact with the oxidizing solution, washed and wiped. This phase of the phenomenon requires further study, but at the present time it does not appear probable that the induced passive condition can be maintained on the surface to an extent that would make it of practical value for treating structural steel. With regard to the preservation of boiler tubes, and for certain special purposes, it is still a question whether a practical application of these principles will be found.

In conclusion, it may be said that there is reason to hope that the time is not far distant when specifications may be drawn for material that is going into service under conditions which make it particularly subject to corrosive influences. The possible added cost of such specially resistant metal will be small in comparison with the benefits which will be derived from its use in the long run.

DISCUSSION.

Dr. M. W. Loeb: The speaker's experiments are so striking an evidence of different polarity at various parts of the metal that I should like to have him explain more fully his statement as to the cause of such polarity in the presence of water. First, how can differences of electro-conductivity influence the positive or negative condition of iron? The speaker states that different quantities of manganese would increase or decrease electro-conductivity. Assuming this to be true would not necessarily produce either polarity or a tendency toward polarization, save through some external source of electricity. Secondly, the speaker assumes these local differences of electro-conductivity to result from the unequal distribution of manganese throughout the mass. Since it is notorious that the presence of manganese toughens an iron, I should think that such toughness would be an indication of homogeneity, rather than segregation. Thirdly, the speaker

considers steel produced by the old processes superior in homogeneity to the Bessemer or open hearth varieties, stating that puddling would produce a more even mixture. I cannot understand how anybody familiar with puddling could consider that the mechanical handling of semi-solid lumps is likely to produce as uniform a mixture as the Bessemer process, wherein the liquid iron dissolves the ferro-manganese and is immediately stirred by a powerful air blast. The cementation process was surely less adapted to uniformity of composition, and we all know how the damascened sword-blades are intentionally stratified, and yet they do not seem ever to suffer from rusting, as would have been expected according to the speaker's premises.

Dr. A. S. Cushman: What I mean to point out is that the differences of potential maintained on the surface of the rusting iron are extremely small. They have been shown to exist by W. H. Walker in a paper recently published in the Journal of the American Chemical Society. It is perfectly reasonable to believe that points or nodes of varying electrical resistance on the surface of iron would lead to differences of potential when the surface is in contact with an electrolyte. If, on the other hand, the conductivity was the same at all points it is unlikely that differences of potential could be maintained. In the latter case rusting would go on slowly and evenly over the surface, and the pitting effect would not be produced. It is this pitting effect, due to local electrolysis, which is particularly harmful and dangerous.

In regard to the point raised, that the old wrought irons of thirty years ago are not more resistant to corrosion than the modern steels, I can only say it would be idle for me to enter into a discussion of this point. It is, I think, the general concensus of opinion that such is the case. And I may state that my own observation has made me believe this to be so. I will remind you of the old forged nail of which I have already spoken, which has been in service in an exposed place for more than one hundred years, and is still in as good condition as the day it was made. It is a matter of common observation that the steel nails made to-day would not last more than a very few years under similar conditions.

MEMOIR
ON THE METHODS OF TREATMENT OF SIMPLE AND COMPLEX ORES

OF

MOLYBDENUM, TUNGSTEN, URANIUM, VANADIUM

BY

GUSTAVE GIN

Part I.—Molybdenum.

Translated by Jos. W. Richards and W. S. Landis.

This Memoir was awarded the Frenzel Prize by the American Electrochemical Society.

Preliminary Observations.

I will take up the processes of treatment of the ores in question in the present memoir according to the normal order of metallurgical operations:

A—Concentration and purification of the ores.

B—Treatment of the concentrates for the extraction of the metals.

C—Refining of the metals.

These operations, and especially the first, which is not altogether indispensable, present at times great difficulties, for they must be carried out on ores almost always complex, containing metals with similar properties and bodies susceptible of forming with these metals very many compounds.

The methods of operation, therefore, take place in numerous stages, repeated precipitations and solutions, or, reducing and oxidizing fusions, alternating with attacks, solution and precipitation by the wet way.

The intervention of electric energy being absolutely necessary for the extraction and refining of the metals, it results that the commercial treatment of the ores in question should be carried out as far as possible in works using water-power as the prime mover, so as to reduce the cost of the electric current. These conditions being present, it is advisable to restrict as far as possible the rôle of electricity and then apply it to certain operations which cannot be achieved by non-electric methods. It is often possible by the use of electric energy to simplify rather complex operations and to accomplish easily reactions which would be impossible by the ordinary chemical methods.

The above considerations will explain the general tendency of the methods to be described, in which I have sought as far as possible to utilize the electric furnace.

Finally, as a classification passing from the more simple to the more complex, I propose to offer the following order:

Molybdenum, Tungsten, Uranium, Vanadium.

The electric furnaces will be described and their function will be explained for only one of the metals cited, because the repetition of the description for each metal would be superfluous.

MOLYBDENUM.

Ores.—The two minerals most common in nature are:

Molybdenite: MoS_2, the bisulphide of molybdenum.
Wulfenite: $PbMoO_4$, molybdate of lead.

Among the other ores which play a less important rôle metallurgically, but as stated should not be completely neglected, may be cited:

Molybdite: MoO_3, molybdic acid.
Ilsemannite: Mo_3O_8, the blue oxide.
Molybdurane: $UO_2.UO_3.2MoO_4$, molybdate of uranium.
Molybdoferrite: $FeMoO_4$, molybdate of iron.
Peteraite: $FeCoMo_2O_8$, molybdate of iron and cobalt.
Eosite: $Pb_3V_2MoO_{16}$, Vanadomolybdate of lead.
Achrematite: $3(Pb_3As_2O_8 + PbCl_2) + 4(Pb_7MoO_5)$, arseniomolybdate of lead.

Finally the slags of the Mansfield copper works contain a considerable proportion of molybdenum, up to 10% and over.

On treating the complex uranium and vanadium minerals there is often obtained residues containing molybdenum in the state of phospho-molybdate of ammonia, or an alkaline molybdate. The products thus saved become valuable only when they accumulate on a sufficiently large scale to permit of industrial treatment.

MOLYBDENITE.

Molybdenite, formula MoS_2, is a gray mineral analogous to graphite, with which it was for long confounded. It is obtained at times in flat hexagonal crystals, but more often in leaves or sheets of a dark lead-blue color with metallic luster. It has a smooth feel, is flexible without being elastic, is easily scratched by the nail and leaves a light metallic gray streak on porcelain.

Molybdenite frequently accompanies tin-bearing pegmatites, granites and zirconiferous syenites. It is often met with in thin layers in the breaks in compact quartz. It is usually disseminated in ribbons or nodules in rocks, rarely in veins.

Occurrences.—Molybdenite is found in the following associations:

Norway—The amphibole gneiss of Arendal, the Glekkeffjord mines.

Sweden—The Isle of Ekholmen, in the Archipelago of Westerwick.

Austria—The tin-bearing quartzes of Zinnwald and Schlangenwald.

Italy—Machetto, Quittengo Biella, Traversella.

Saxony—Auerbach, Altenberg, Ehrenfriedensdorf.

India—Chutia Nagpur.

Australia—Elsmore, Clackline Coolgarie, Kingsgate.

United States—Molybdenite has been noted in the following mines:

Ophir and Dillon (Montana).
Haddam and Saybrook (Connecticut).
Cooper (Washington).
Blue Hill Bay (Maine).
Pitkin and Rock Creek (Gunnison County, Colorado).
Shutesberg and Burnfield (Massachusetts).

Warwick (New York).
Westmoreland (New Hampshire).
The most of these mines furnish only small quantities.

Canada—Molybdenite has been found in New Brunswick, Ontario, Province of Quebec and in British Columbia. (Giant Rossland Camp Mines.)

Newfoundland—Recontre, Fortune Bay.

France—
Chessy (Rhone).
Vaulvry (Haute Vienne).
Chillot (Vosges).
Meymac (Correze).

Analyses:

	Australia. (Gin.)	Sweden. (Gin.)	Canada. (Gin.)
MoS_2	97.70%	98.04%	81.16%
As_2S_3	0.52%	0.21%	0.28%
Cu_2S	0.64%	0.16%	0.44%
SiO_2	0.96%	1.67%	12.60%
Al_2O_3	0.10%	.....	1.65%
P_2O_5	0.7%	.....	0.04%

There may be found at the conclusion of this memoir on molybdenum an analysis of a molybdenum ore much less pure than the above.

Wulfenite or Melitose ($PbMoO_4$).

Properties.—This mineral, found for the first time in Antiguoia, is often in the form of tabular crystals, of square section, or in truncated octahedrons, color wax yellow or honey yellow, luster brilliant. It has been reproduced artificially in the form of large square transparent crystals of a yellow color by melting molybdate of soda with chloride of lead in the absence of air. Its specific gravity varies between 6.3 and 6.9, the hardness is 3. It decrepitates before the blowpipe and melts easily.

Occurrences.—It is found with other lead minerals at Bleiberg (Carinthia), Przibram (Bohemia), Badenweiler (Baden), Annaberg (Saxony), Meymac (Correze), Southampton (Massachu-

setts), the Troy Manhattan Copper Co. and a mine at Mammoth (Arizona).

There are a number of less important occurrences of the mineral in the lead mines of Mexico, Peru and Chili.

Analyses:

	Mexico. (Damour.)	Chili. (Gin.)
Molybdic acid	28.92%	31.80%
Phosphoric acid	2.80%	0.70%
Carbonic acid	.....	2.00%
Lead	53.56%	58.40%
Gangue	12.80%	8.00%

Molybdite or Molybdenum Ocher (MoO_3).

Molybdite is the natural molybdic acid found in fibrous or pulverulent masses of a straw-yellow color and a silky luster. Specific gravity is 4.5. It is quite soluble in hydrochloric acid. It crystallizes in orthorhombic prisms and is isomorphous with valentinite. It is found in the Tyrol and in Sweden, associated with molybdenite.

Ilsemannite is a molybdate of molybdenum, blue or bluish-black in color, easily soluble in water, and is formed from the alteration of metallic molybdenum.

Molybdurane is a molybdate of uranium, found at Joachimsthal and in Colorado.

Concentration and Purification of Molybdenum Minerals.

Molybdenite is found generally in a state of considerable purity and not rarely it may be employed directly in metallurgical operations, some molybdenite ore from Australia assays up to 97 per cent. MoS_2. It is, however, frequently associated with quartz in acid rocks and compounds of other metallic sulphides so that it is impossible to separate them from it in a satisfactory manner by mechanical or electrostatic means. When this ore is submitted to a reducing fusion there are formed silicides and arsenides of molybdenum and all other metals, the presence of which may be prejudicial to the commercial value of the products. If on the other hand the mineral is melted with alkali, the silica is attacked

and the subsequent leaching forms silico-molybdates, which interfere with the final purification.

On the other hand, the naturally pure molybdenite contains almost always arsenic and phosphorus, sometimes in sufficient proportions to make a preliminary chemical purification obligatory, such as precipitating the phosphorus and arsenic first in the state of phospho- and silico-molybdates.

In such minerals as wulfenite, where the molybdenum is associated with another metal, whose presence would be useless or prejudicial in the industrial product, it is indispensable to eliminate those metals to utilize their commercial values or simply to get rid of them.

Mechanical Concentration.—The average content of molybdenite in rocks in the form of bands or nodules is generally quite small and necessitates mechanical concentration before shipping to the reducing works.

Separation by Means of Sieving.—I. W. Wells has devised a process based on the plasticity of molybdenite, which is flattened out when it is passed between cylindrical rolls, while the brittle gangue is pulverized. After being thus crushed it is sieved and only the flakes of molybdenite remain on the sieve. On a certain ore containing 6 per cent. molybdenite, concentrates containing 50 per cent. were made, but the loss is always considerable.

Separation by Electrostatic Means.—A process which appears to have a great future is the electrostatic separator devised by Professor Blake, of Kansas, and designed commercially by Messrs. Morscher and Swart, of Denver, Col. It is designed particularly for ores which are not suitable for the hydro-mechanical or magnetic separation, and is based on the following principles:

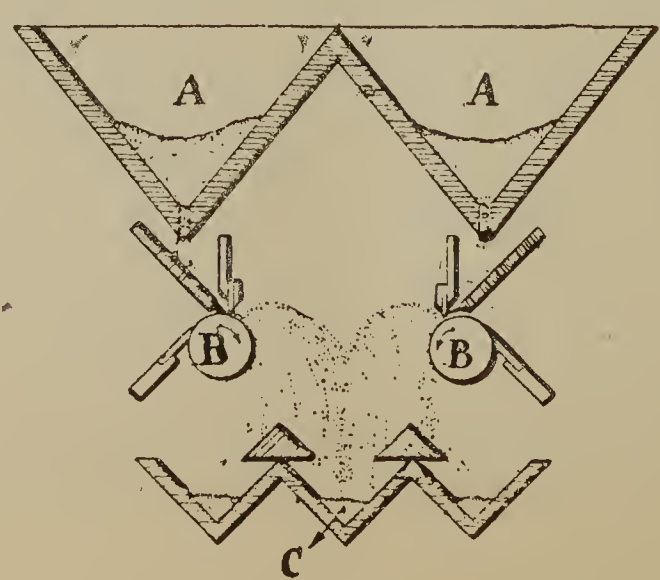

FIG. 1.

If a solid particle is close to a body possessing an electric charge it tends by induction or by contact to acquire the potential of this body. During the charging the particle is attracted to the electrified body, then it is repelled when it has attained the same potential. It is the classical phenomenon of the pith ball of Coulomb. But this repulsion is exerted at the end of a variable time, depending on the capacity of the particle.

A pulverized mixture submitted to the action of a charged electrified body will possess for each of its particles a time factor characterizing the duration of its adherence to the charged surface. This time factor is almost nothing for good conductors, but may reach several days for di-electrics. Admitting this, we can see that if a fine layer of the powder glides down a metallic inclined electrically charged surface, the particles will fall off in certain zones characteristic of each of the minerals contained in the ore, by reason of their being electrified and repelled in the order of their electric conductivity and capacity.

The practical application of this principle is as follows:

The mineral is pulverized and fed in a thin layer by the shaker A on two metallic cylinders B, forming the repelling poles and which are continually rotated. These poles are charged by a 350,000 volt current, generated by the system of Wagner. The cylinders are cleaned continually by a brush which detaches the adhering particles. As is seen from the figure, only the conducing particles are thrown out into the central receiver C, from which they are removed by a screw-conveyer. The non-conducting particles fall into the lateral funnels. With this electrostatic Blake separator concentrates up to 60 per cent. molybdenite may be made from ores containing only 3 per cent. The separator treats from 10 to 15 tons of ore per day and requires three horse-power.

Concentration by Flotation—The Elmore Process.—This process, called by the author the "Vacuum Flotation Process," rests on the principle that oil in a mixture of water and very fine particles of minerals adheres to the minerals and not to their gangue. In some cases this selective action of the oil is increased by the addition of small quantities of acid. Finally, by reducing the pressure above the liquid to a vacuum one can extract particles of air which are dissolved in the water, and these attach

themselves to the crushed particles of the mineral, aiding thus in floating them to the top. The apparatus is shown in Fig. 2.

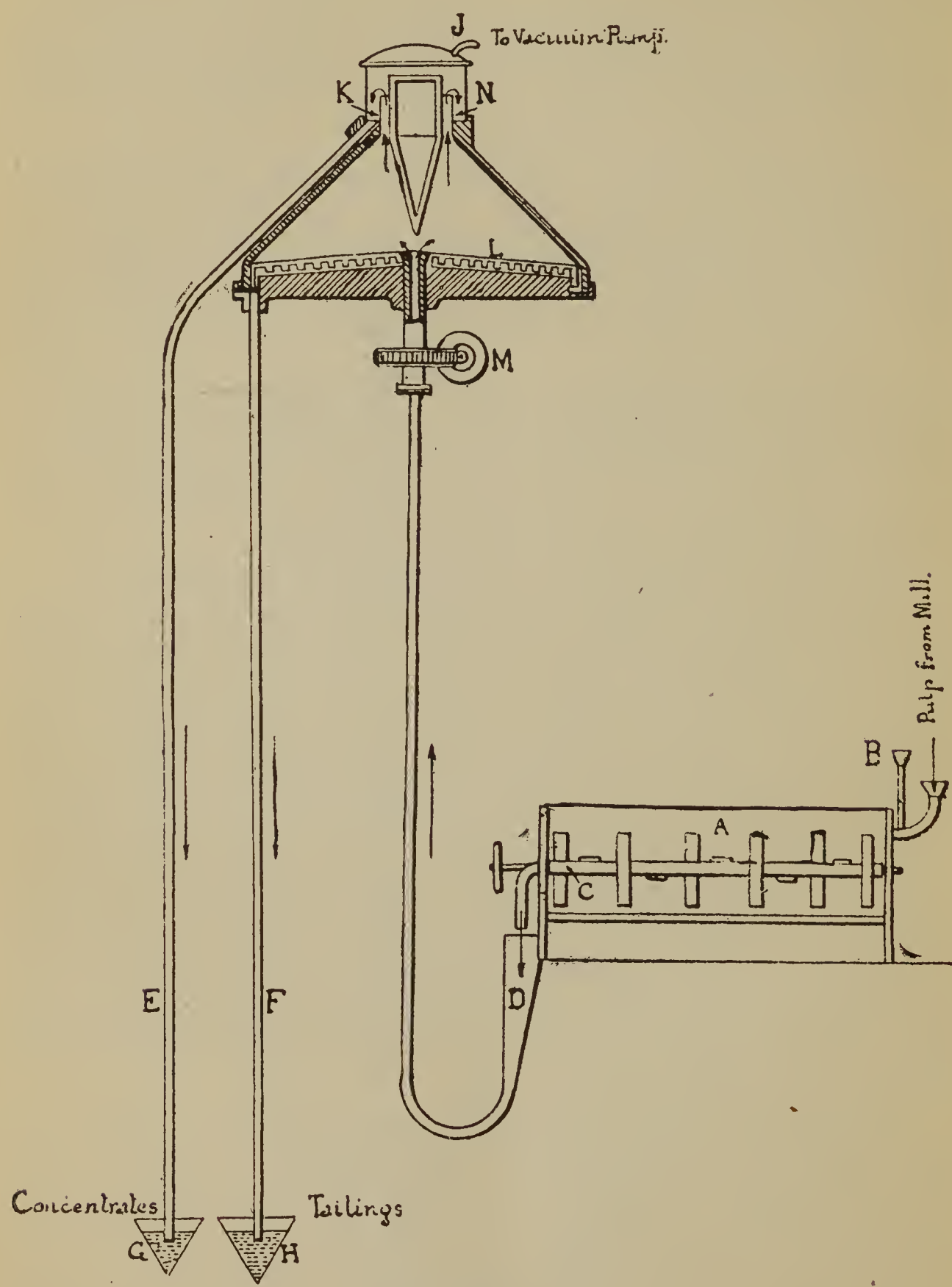

FIG. 2.

In the mixer A are arms making from 30 to 40 revolutions per minute; the slimes, water, oil and acid are introduced at B. The

mixture flows continually into D and is sucked up into the receiver I, which is connected by the tube J. The liquid passing into the canal K flows into the tube E, carrying the concentrates into G. The ungreased particles rest at the bottom of I, where they are agitated by the propeller L and flow finally through the tube F into the bin H. The tubes E and F being longer than D form a sort of siphon, causing the automatic flow of the solution. The apparatus is provided with a window at K, through which the progress of the concentration may be observed. The tube D is generally 7.5-9 meters long for an apparatus in which the reservoir I is 1.5 meters in diameters; the motive power is 2-2.5 horse-power for pump, separator and mixer. The price of the separator complete F. O. B., London, is $1,750. An apparatus 1.5 meters in diameter will treat 35-40 tons of mineral per day. The quantity of oil and acid used varies from 1.5-4.5 kilograms per ton of ore treated. Almost any oil may be used, such as the heavy oil of California, Texas, Russia, Borneo, olive oil residues, kerosene, tars or fish oils.

Although this process cannot be applied to all ores, its use is very extensive and it ought to be quite satisfactory. It is best used only for those ores whose concentration by the ordinary processes is very difficult or impossible. The process is in regular operation in a number of places.

Ores of molybdenite with feldspar gangue containing 3.4 per cent. molybdenum have been concentrated to 40.8 per cent., with the tails 2.25 per cent; the concentrates containing 93.5 per cent. of the useful mineral.

Chemical Purification of the Concentrates.

Mechanical enrichment of the poor ores is generally followed by a chemical concentration. All the industrial chemical processes for the purification of molybdenum ores are based on the following principles. If molybdenum is associated with earth metals the material is fused with an alkaline carbonate, dissolved in water and filtered to separate out the alkaline earth carbonates. When the molybdenum material contains various metals it is dissolved in an acid solution and all the metals belonging to the two first groups are separated out by H_2S. The separation of molybdenum from the metals of the second group is made by means of an

alkaline sulphide. To separate molybdenum from phosphorus and arsenic the solution is made alkaline with ammonia and the phosphorus and arsenic precipitated as ammonia-magnesium phosphates or arsenates. Afterwards by saturating the solution with H_2S the molybdenum is transformed into a sulpho-molybdate from which the trisulphide may be precipitated by acids.

Minerals containing molybdic anhydride or a molybdate may be treated with gaseous hydrochloric acid forming molybdic hydrochloride, which dissolved in water yields molybdic acid on evaporation.

The whole industrial chemistry of molybdenum is condensed in these few principles, for if metallurgical products are the aim of the manufacturer it is useless to eliminate the small quantities of tungsten, tantalum and niobium which are most always associated with molybdenum ores. These impurities, from the metallurgical point of view, play a part which is not injurious to the molybdenum and therefore there is no object in eliminating them.

Manufacture of Molybdic Anhydride from Molybdenite.

Berzelius' method.—The ore is roasted in an oxidizing atmosphere without becoming above a red heat and the roasting prolonged until no more SO_2 is set free. The roasted material, which looks like an earthy-yellow powder, is cooled and treated with ammonia solution of 20° Baume (sp. gr., 0.935), which dissolves the molybic acid. The filtered solution is then evaporated, during which operation some of the impurities precipitate; but the concentration must not be pushed too far, or the molybdate of ammonium will precipitate itself into crystals of a composition of $Mo_7(NH_4)_6O_{24} + 4H_2O$. The solution is filtered hot, ammonia is added to replace that which is evaporated, and then concentrated down until crystals of ammonium molybdate separate out. The crystals are calcined below low redness. The mass becomes gray, then brown, afterwards bluish, but becomes yellow again by further oxidation. The product obtained is often impure, retaining phosphoric and arsenic acids.

I have modified the above method of operation as follows: I give the molybdenite an oxidizing roasting until no more SO_2 is disengaged. The product is then fused with sodium carbonate, forming molybdate, phosphate, silicate, arsenate, sulphate and

aluminate of soda. Taking up with water, there is formed phospho-molybdate, silico-molybdate and arsenio-molybdates. I then have tried to introduce some carbonate of ammonium to precipitate all the phospho-molybdic acid, but I have found it preferable, when desiring very pure molybdic acid, to first treat the solution with H_2S, transforming the molybdate of sodium into sulpho-molybdate,

$$Na_2MoO_4 + 4H_2S = Na_2MoS_4 + 4H_2O,$$

while the silica and alumina are slowly precipitated. The red liquor obtained is filtered and hydrochloric acid added until the molybdenum trisulphide is completely precipitated as a dark, brownish, gelatinous precipitate. This is let stand several hours and filtered, phosphoric acid remaining in solution, while the precipitate is free from it. The precipitate is filtered out, dried, heated to redness in the absence of air in a crucible placed in a muffle furnace which connects with a cool condensing chamber. Any arsenic sulphide present is sublimed, and the trisulphide of molybdenum loses sulphur and becomes a bisulphide. The latter is then roasted at low redness in a muffle in a current of air, and when SO_2 is no longer evolved a little nitric acid is sprinkled upon the mass to finish the oxidation. Molybdic acid thus obtained is quite pure, excepting for a little silica which may be present. To eliminate this, it is necessary to transform it into ammonium molybdate, which when dissolved in water leaves silica behind and can be evaporated and calcined. The silica may also be eliminated by boiling the impure molybdic acid with magnesium carbonate until CO_2 is no longer evolved. Insoluble magnesium silicate is thus formed and soluble neutral magnesium molybdate, $MgMoO_4.5H_2O$. The silica is separated by filtration; the solution is concentrated, and on cooling, colorless transparent crystals of a prismatic form are obtained. The molybdic acid may be obtained from these by dissolving them in hydrochloric acid or treating the solution with this acid together with a few drops of nitric acid.

Simplified method.—The production of molybdenum for metallurgical purposes does not always require such rigorous purification, and the following process may be used, thus avoiding the complications of the previous ones: The ore is roasted at a low red heat in an oxidizing atmosphere, the dirty

yellow powder obtained is digested with concentrated ammonia in excess, which will keep in solution any phospho-molybdate of ammonium formed. After filtering, a calculated quantity of magnesium chloride is added sufficient to precipitate the phosphoric and arsenic acids present as magnesium ammonium phosphate or magnesium arsenate, leaving in solution ammonium molybdate mixed with ammonium chloride. The filtered solution is evaporated, crystallized and calcined for MoO_3 or MoO_2.

Distillation of Molybdic Anhydride.

In the working channels of the circulating induction furnace, to be described further on, the material to be treated is placed on a resistor bath of copper. The material being raised to bright redness, molybdic acid distills off and is condensed in a condensing chamber. This remarkably simple operation can be carried out only in an electric induction furnace, which allows of the operation in a closed space without electrodes and under neither reducing nor oxidizing reaction.

Treatment by Alkaline Polysulphides.

Molybdic acid or other oxides of molybdenum may be obtained from molybdenite with the total elimination of silica, phosphoric acid and arsenic acid by a purely chemical method. Potassium polysulphide is allowed to act upon molybdenite, producing a sulpho-molybdate in solution, and from which the trisulphide can be precipitated; the latter is oxidized to molybdic acid, transformed into ammonium molybdate and calcined for molybdic dioxide. The details of this process, according to Berzelius, are as follows:

In a graphite crucible is placed a mixture of potassium carbonate, sulphur and charcoal dust in proportions suitable for forming potassium tetra-sulphide according to the reaction,

$$(1) \qquad 6K_2CO_3 + 25S + 2C = 6K_2S_4 + SO_2 + 8CO_2.$$

Molybdenite is added to the mixture in mass or fine powder and in the proportions indicated by the following reaction:

$$(2) \qquad 4MoS_2 + 2K_2S_4 + 2K_2CO_3 + S = 4K_2MoS_4 + 2CO_2 + SO_2.$$

The complete reaction from the original substances may be stated as follows:

$$(3) \qquad 6MoS_2 + 6K_2CO_3 + 14S + C = 6K_2MoS_4 + 7CO_2 + 2SO_2.$$

The crucible is then filled with powdered charcoal and heated to 400° C. to obtain the reaction (1), which does not require a high temperature. When the blue flame coming from the combustion of the sulphur ceases, the temperature is raised to redness, to decompose the potassium sulphate which may have been formed. When no more sulphur dioxide escapes, the temperature is raised to whiteness and kept there several hours. The crucible is cooled out of contact with air, the black porous mass is broken up and digested with boiling water. The liquid is filtered rapidly, evaporated in a closed oven at a low temperature, and then concentrated hydrochloric acid is added, to precipitate the brown molybdenum trisulphide, which becomes black when dry. This product is roasted to oxide, as has already been explained.

Manufacture of Molybdic Acid from Wulfenite.

Several methods have been proposed. The process of Elbers consists in attacking small amounts of wulfenite with concentrated sulphuric acid. The mass is heated and constantly stirred until sulphuric acid commences to come off, then cooled and diluted with cold water. The residue contains the lead as sulphate. The blue solution is filtered off; it contains the molybdenum as MoO_2SO_4.

The solution is evaporated after the addition of some nitric acid, the dried residue is washed with water acidulated with nitric acid, which dissolves the phosphoric acid and also a small quantity of molybdic acid, but the latter may be saved by repeating the above operations.

Christl fuses the finely-ground lead molybdate with an equal quantity of sodium carbonate in an iron crucible, forming oxide of lead and carbonate of soda, which latter can be decanted from the former. The molybdate is dissolved in water, and with the addition of some nitric acid is evaporated to dryness. The sodium nitrate formed is separated from the molybdic acid

by washing. This process is not very convenient and requires iron crucibles, since earthen crucibles are immediately attacked by the lead oxide.

Mixed method.—Forced by the necessity of using scanty apparatus, I have modified as follows the method of Christl, using in the first instance an electrothermic reduction. The lead molybdate is mixed with sodium carbonate and a proper proportion of carbon and fused in an electric furnace. The lead and any copper present are reduced to the metallic state, leaving a slag of molybdate of sodium contaminated with arsenate, aluminate, silicate and phosphate of sodium. This slag is cooled and broken up, pulverized, treated with boiling water, and the molybdic acid extracted from the solution by the methods already explained for the treatment of molybdenite.

It is usually sufficient to add small quantities of ammonia and magnesium chloride to the solution to precipitate phosphoric and arsenic acids as insoluble magnesium or ammonia-magnesium phosphates or arsenates.

Variations of the preceding methods.—All the lead molybdates are made by mixing with magnesia or magnesium carbonate and melting in an electric furnace, resulting in a magnesium slag. The latter is finely pulverized and treated with boiling water, which dissolves, though only to a slight extent, the magnesium molybdate. The filtered liquid gives, on cooling, transparent prismatic crystals containing five molecules of water of crystallization.

I have called attention to this simple process because the salt obtained, unchangeable in air, fusible only at 1440° C., may be used directly for the production of cast molybdenum, by means which I will describe further on, without the necessity of transforming it into MoO_2. The residue left after the lixiviation with water always contains a small quantity of undecomposed molybdenum.

Preparation of Molybdic Acid, Involving the Production of Cast Molybdenum.

It may appear paradoxical, yet this process is capable of being practiced as economically as those preceding it, when the electrothermic reduction can be obtained in a works using electric

energy at low cost. In this case, the first reduction by electricity may be regarded simply as a first concentration, intended to eliminate the larger part of the silica and other impurities.

The process consists in making a coarse cast metal, starting with unpurified ore, either natural molybdenite or roasted molybdenite. The cast metal obtained is broken in pieces and roasted in a muffle externally heated and traversed by a current of heated air and communicating with a condensing chamber. The air oxidizes the metal, which burns without flame, producing, if the temperature is above 1300°, molybdic acid, which sublimes and is caught in the condensing chamber. All of the molybdic acid is not expelled, and there remains in the muffle a mixture of molybdic acid and silica, which may be extracted by ammonia, and the molybdic acid may then be recovered by one of the preceding methods. The direct distillation of molybdic acid formed by the oxidation of molybdenite is far more economical and simpler than the method to be next described.

Distillation Process Based upon Molybdenum Hydrochloride.

The following process furnishes MoO_3 or MoO_2 of high purity. Roasted molybdenite, or any pulverized molybdate heated up to 400° C., is submitted to the action of a current of dry hydrochloric acid gas. There is formed molybdenum hydrochloride, $MoO_3.2HCl$, volatile above 250° C., but which is caught in water, in which it is very soluble. When the solution has become sufficiently concentrated, it is evaporated, furnishing thereby hydrochloric acid and precipitating molybdic acid. When put into a practicable form, this process has the advantage of simplicity, avoiding all the complicated operations usually necessary for the elimination of impurities.

Transformation of Molybdic Acid into Molybdenum Dioxide.

Molybdic acid cannot be treated directly in an electric furnace, because of the low temperature at which it sublimes; it is necessary, therefore, before reduction to convert it into the dioxide. The most convenient process is that of Bucholz, which

consists in calcining ammonium molybdate in a reducing atmosphere. The transformation is not complete, 10-15 per cent. of undecomposed molybdate remaining. On the other hand, the molybdous oxide obtained contains a little nitrogen, which exercises no injurious influence, since the nitrides of molydenum are dissociated at redness. Total decomposition may be obtained by adding to the ammonium molybdate carbon sufficient to produce the following reaction:

$$(NH_4)_6Mo_7O_{24} + 4H_2O + C = 7MoO_2 + 7H_2O + 3NH_4 + 3N + 7CO.$$

Molybdous oxide may also be obtained by the action of metallic zinc on molten sodium molybdate:

$$Na_2MoO_4 + Zn = Na_2ZnO_2 + MoO_2.$$

The crystalline bluish violet product is washed with a solution of soda and then with hydrochloric acid to separate out the zinc compounds.

Molybdous oxide may also be obtained by fusing molybdic acid or an alkaline molybdate with pulverized calcium carbide:

$$6MoO_3 + CaC_2 = CaMoO_4 + 5MoO_2 + 2CO_2.$$

The mixture of molybdous oxide and calcium molybdate can be directly utilized in the electric furnace for reduction by carbon, or in a refining furnace for the elimination of silica from crude molybdenum by the action of the oxide.

Electrolytic Preparation of the Intermediate Oxide.

The blue intermediate oxide, Mo_2O_5, can be obtained by the electrolysis of molybdic acid. The resultant product crystallizes in copper-colored crystals, which rapidly become blue in air. This process is not above criticism, for molybdic acid being volatile at redness, the loss by volatilization may be quite high. To avoid this volatilization, it is preferable to electrolyze potassium molybdate, which gives directly Mo_2O_5. The electrolyte is made by melting together 15 parts of molybdic acid with two parts of potassium carbonate, producing a salt corresponding approximately to potassium penta-molybdate, $K_2O.(MoO_3)_5$. This molten molybdate has a very low vapor tension, and losses from it by volatilization are very small. When molten, it is

a good conductor, and after passing the current some time, the latter passes with less resistance, without producing any further sensible electrolysis. A better electrolytic output is obtained by adding to the electrolyte a less-conducting salt, whose heat of formation is much higher, in order that it may not be decomposed by the current. Potassium fluoride, in the proportion of four parts of the fluoride to six parts of the molybdate, gives good results. The electrolysis being finished, the material is cooled, pulverized, and washed with water containing some ammonium chloride, to prevent the precipitation of the blue oxide.

Preparation of Pure Molybdenum.

1. Reduction of Oxides of Molybdenum by Hydrogen.

The reduction of molybdic acid by hydrogen was proposed by Wöhler and Rammelsberg. It was used by Debray,[1] in 1868, for the obtaining of the pure metal for the determination of the atomic weight of molybdenum. The molybdic acid is reduced by hydrogen at the lowest temperature possible, so as to obtain the non-volatile red oxide. This dioxide is then reduced by continuing the operation at a higher temperature.

Guichard[2] has made further studies of this method. Above 500° C. the MoO_2 is reduced to Mo by hydrogen. It commences to lose oxygen at 500° C., but the reduction is very slow; at 550° C. the reaction is more marked; at low redness it rapidly takes on a metallic appearance; at 1000° C. the reaction is rapid and complete.

Now that the manufacture of electrolytic hydrogen in connection with that of oxygen has become commercialized, the manufacture of powdered molybdenum may be easily taken up as a means of utilizing the hydrogen, using closed retorts, like gas retorts, heated to bright redness by an external fire or by the passage of an intense electric current. The retorts cannot be of silicious material, since molybdenum attacks silica at a yellow heat; they are best made of alumina, mixed with calcium fluoride and baked at a high temperature.

2. Reduction of the Oxide by Means of Aluminium.

Stavenhagen has proposed using aluminium in the presence

[1] Compt. rend., **66**, 732 (1868).
[2] Compt. rend., **124**, 102 (1897).

of liquid air as a reducing agent for molybdic acid. The output of this method is poor.

The idea works better using powdered aluminium and calcium molybdate and starting the reaction by the Goldschmidt method.

3. Reduction of Molybdenum Chloride by Hydrogen.

Wöhler and Uslar pass a current of hydrogen over molybdenum penta-chloride placed in a tube heated to redness. The metal was deposited on the sides of the tube as a brilliant steely-gray mirror, capable of being detached and hammered out.

4. Reduction by the Electrolytic Formation of Amalgam.

Feree[3] has prepared molybdenum amalgam by electrolyzing a solution of molybdic acid in hydrochloric acid, using a platinum anode and a mercury cathode. The amalgam obtained had the composition $MoHg_9$, and by compression could be converted into another amalgam richer in molybdenum.

5. Electrolytic Manufacture of Pure Molybdenum.

Molybdenum penta-chloride can be electrolyzed, but it is very deliquescent and difficult to handle and preserve. It melts at 194° C., boils at 270° C., and its low physical stability is an obstacle to its industrial use. On the other hand, the double chloride of molybdenum and sodium is much more stable, less deliquescent, has a melting point above 300° C., and does not sensibly give off vapors below redness. Its specific electrical resistance is about 0.52 ohm (per centimeter^3). It can be easily electrolyzed and furnishes molybdenum free from carbon.

To prepare the double chloride, an inclined muffle is used, made of a refractory aluminous earth, and at one extremity is placed common salt, at the other extremity, pulverized molybdenum carbide or cast molybdenum carbonized sufficiently to have been easily granulated. On heating to redness and passing a current of chlorine through the retort, the metal is rapidly attacked, forming volatile molybdenum penta-chloride, which is absorbed by the sodium chloride, the latter becoming dark brown and liquefying rapidly. The double chloride, as it is formed, runs down into a closed receiver of enameled iron and cooled by circulating water. When all the molybdenum is consumed, the retort is cooled and the water-cooled vessel

[3] Compt. rend., 122, 733 (1896).

opened, furnishing an amount of double chloride which is at once placed in tightly-closed boxes.

The electrolysis of the double chloride is effected in a furnace similar to the one I described in 1902 for the manufacture of vanadium.

Electric Furnace for Producing Molybdenum.

The electric furnace I have used for the electrolytic production of molybdenum differs very little from those at present used for

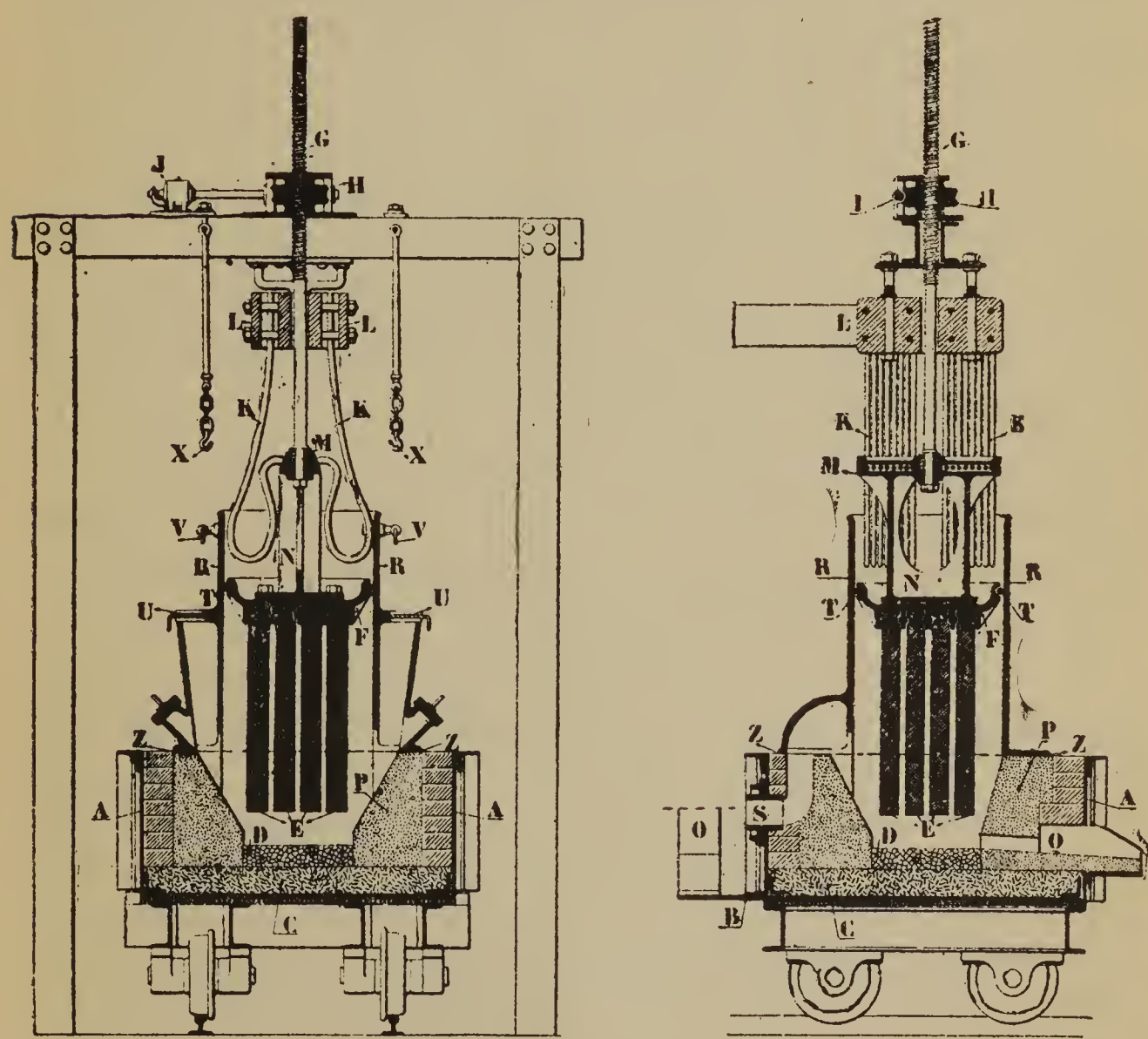

Fig. 3.

the production of aluminium. It is composed essentially of a sheet-iron crucible A mounted on wheels; the bottom B bears a layer of molybdenite C, as pure as possible, forming the intermediate conductor between the metallic sides and the cathode proper, which latter may be formed of powdered molybdenum compressed into place, or by a bath of melted lead.

The layer of molybdenite may be replaced by pure crystallized molybdenum dioxide obtained by the electrolysis of fused anhydrous molybdic oxide. This material, when agglomerated, is sufficiently conducting and refractory to meet the conditions. The anode is a bundle of carbons E, separated from each other by a space of some centimeters to facilitate the evolution of gas. The electrodes are carried on a holder F, being fastened thereupon by casting bronze around them, which assures a perfect electrical connection. The anode is raised or lowered by a screw G, moving in a nut H, the latter being turned by a worm I, driven by an electric motor J.

The current reaches the anode by the flexible cables K, connected at L with the positive bus-bar and at M with a conducting piece N, which is fastened by the nuts to the head F of the anode. The cathode is connected with the negative bus-bar by means of the copper plates O. The interior of the crucible is lined with agglomerated alumina P. Q is a tap-hole for taking out the metal or the exhausted bath.

The crucible is completely surrounded by the envelope R to keep the gaseous products from coming out into the atmosphere; it is provided with a conduit S, connecting with a flue. A sheet-iron cylinder T completes the envelope for catching the gases.

The mixture to be electrolyzed is introduced through openings U, which are furnished also with peep-holes, through which the bath may be observed. When it is necessary to replace an electrode, the anode, with its cover, is lifted until the cover can be suspended by the hooks X, then the anode is lowered, the cover being suspended, and the replacement made. Similarly, the lower part, containing the cathode, can be wheeled away and a new one put in its place, the joint Z being made with fire-clay.

Lining of the Furnace.—Moulded bricks are made from a mixture of alumina and calcium fluoride, 90 parts of pure alumina and 10 parts of powdered fluorspar, somewhat moistened with hot tar to give it plasticity, and then strongly compressed hydraulically into moulds. The bricks thus obtained are given a prolonged heating to redness in a reverberatory furnace, slowly cooled to avoid cracking, when the product obtained is perfectly resistant to the electrolytic bath used. On

laying the bricks, a mortar is used of the same material, tamped in by hand.

To make pure molybdenum, the anode used is carbon, the cathode a bed of fragments of molybdenum, stamped in and resting on a layer of molybdenite, tightly pressed against the copper bottom of the crucible.

The tension used is 9-10 volts, varying with the amount of molybdenum in the bath. The current density should be between 1 and 1.5 amperes per square centimeter horizontal section of the anodes. The superficial current density should not be above 0.8 amperes per square centimeter. The current density at the cathode should be at least 1 ampere per square centimeter.

Calculations for a Molybdenum Furnace Using 8,000 Amperes.

A is the current passing through each anode.

A′, the current from the terminal faces of the anode.

A″, the current from the lateral faces of the anode.

Δ, the current density on the horizontal section of the anode $= \frac{A}{a^2}$

δ, the superficial current density at the anodes.

d, the current density at the cathode.

a, the side of each anode.

e, the distance between the external faces of the anode and the sides of the crucible.

e′, the distance between two electrodes.

H, the distance between the cathode and the terminal faces of the anodes.

h, the distance the anodes are plunged into the bath.

k, the resistivity of the bath.

E′, the drop of e. m. f. due to the ohmic resistance of the bath.

The current issuing from the sides of the anodes towards the sides of the crucible or towards the central space will be

$$A_1'' = \frac{ae'hE'}{k(h^2 + e^2)} - \log\left(1 + \frac{h^2 + e^2}{Hh}\right)$$

For the faces of the electrodes facing each other, we have

$$A_2'' = \frac{ae'hE'}{k(h^2 + e'^2)} - \log\left(1 + \frac{h^2 + e'^2}{Hh}\right)$$

Since the logarithmic term is negligible in comparison with the first term, we may write

$$(2)\quad A'' = 2(A_1'' + A_2'') = \frac{2ahE'}{k}\left[\frac{e}{h^2 + e^2} + \frac{e'}{h^2 + e'^2}\right]$$

Assuming this, we have

$$A'' = A - A' = A - \delta_{max.}\, a^2.$$

Or, we know that the maximum superficial current density at the anodes should not be above 0.8. Using this limiting value, we have

$$A - 0.8a^2 = \frac{2ahE'}{k}\left[\frac{e}{h^2 + e^2} + \frac{e'}{h^2 + e'^2}\right]$$

To apply this equation to a specific case, let us assume the following:

Number of anodes, 8.
Current passing per anode, 1,000 amperes.
Drop of e. m. f. due to ohmic resistance of the bath, 5 volts.
Resistivity of the bath, 0.52 ohms per cubic centimeter.
Depth of immersion of the anodes, 8 centimeters.
Distance of anodes from the sides of the crucible, 14 centimeters.
Distance between the two electrodes, 2 centimeters.

With the above data substituted in equation (3), we have

$$a^2 + 16a - 1{,}250 = 0.$$

Whence

$$a = 28.3.$$

The eight square carbons should therefore be 28-30 centimeters on a side.

Using $a = 28$, the current density per cross-section of anodes becomes 1.27, while the current density at the cathode is 0.79 amperes per square centimeter.

Details of the Electrolysis of the Double Chloride.

The method to be described has two essential disadvantages when used for industrial purposes:

(1) The bath is impoverished as the metal is liberated, making a variation in its running and a discontinuity of the operation.

(2) The chlorine disengaged rapidly attacks the carbon electrodes and all the exposed parts of the apparatus.

I try to remedy the first difficulty by keeping the bath at as nearly constant concentration as possible, adding at small intervals a regular quantity of molybdenum chloride, but this salt, as has been described, is hard to handle and very difficult to preserve. I then substitute for the carbon anodes anodes formed of cast molybdenum obtained by a simple reduction of molybdic dioxide by carbon. This changes the electrolytic method from a method of extraction to one of refining a crude molybdenum. This diminishes the working tension across the electrodes to 6-7 volts, instead of the 9-10 previously required. The evolution of chlorine is stopped; the envelope around the furnace and other appliances for keeping gas out of the furnace room may be dispensed with. The molybdenum obtained is not in a melted state, because its point of fusion is too high, but as a porous deposit which can be detached en bloc from the tamped bottom of the furnace. These blocks can be melted down in an electric furnace, protecting it from contact with the air. Alloys of molybdenum may be obtained in the same furnace by using as cathode the alloying metal. Pure molybdenum without carbon may be manufactured, using as electrolyte the double fluoride of molybdenum and calcium and a cathode of iron. The carbon in the cast molybdenum anodes floats to the surface of the bath, and by its combustion preserves the temperature and reduces volatilization.

Using lead as the cathode, lying upon the floor of molybdenite or molybdenum dioxide as already described, the lead molybdenum alloy is formed and may be run out of the furnace as long as the molybdenum content is not higher than 18 per cent. of molybdenum, corresponding approximately to $MoPb_2$. These two metals appear to have only a very feeble affinity for each other and

may be separated easily by heating in an electric furnace under a layer of melted alumina. The lead distills off and there remains pure molybdenum under the alumina slag, which may then be cast into ingots, taking precautions to keep from air as much as possible.

Preparation of "Cast" Molybdenum.

Process of Guichard.—This process consists of the direct reduction of molybdenite by carbon in the electric furnace.

$$2MoS_2 + 3C = Mo_2C + 2CS_2.$$

The difficulty in the process is the act of obtaining pure molybdenite, for the cast metal obtained naturally contains all the metals or the carbides of the metals present as impurities, as well as phosphorus and silicon from the gangue.

Process of Moissan.—Molybdenum dioxide is reduced by carbon in the electric furnace. The dioxide is obtained by calcining ammonium molybdate in a Perrot furnace, the oxide on cooling being a dense powder of a violet-gray color. It is mixed with carbon and heated in the crucible of a Moissan furnace with a current of 350 amperes at 70 volts, reduction taking place in seven to eight minutes, and cast molybdenum containing 9-10 per cent. of carbon results. By using an excess of the dioxide, a metal with less carbon in it may be obtained. Moissan's furnace is not suitable for continuous industrial use.

Electric Furnace for the Manufacture of "Cast" Molybdenum.

"Cast" molybdenum may be made in a resistance furnace similar to the calcium carbide furnace. The furnace which is about to be described may be likewise employed. It is the most simple form of the multiple furnace which I patented in 1897-98 and with which I experimented at that time in the works at St. Beron in the Savoy. Analogous furnaces were employed in 1899 by the Willson Aluminium Co. Since then they have been reproduced or imitated with more or less important modifications of details. It is probable that this furnace, however, like all those which use carbon electrodes, will disappear before the induction furnace.

The furnace for the production of "cast" molybdenum consists

of a movable crucible A on wheels, upon which is an extension B. In the bottom of the crucible is a fixed electrode C, which serves as an intermediate electrode for the passage of the current between the two movable electrodes E_1 and E_2. The metal passes from one movable electrode to the intermediate fixed

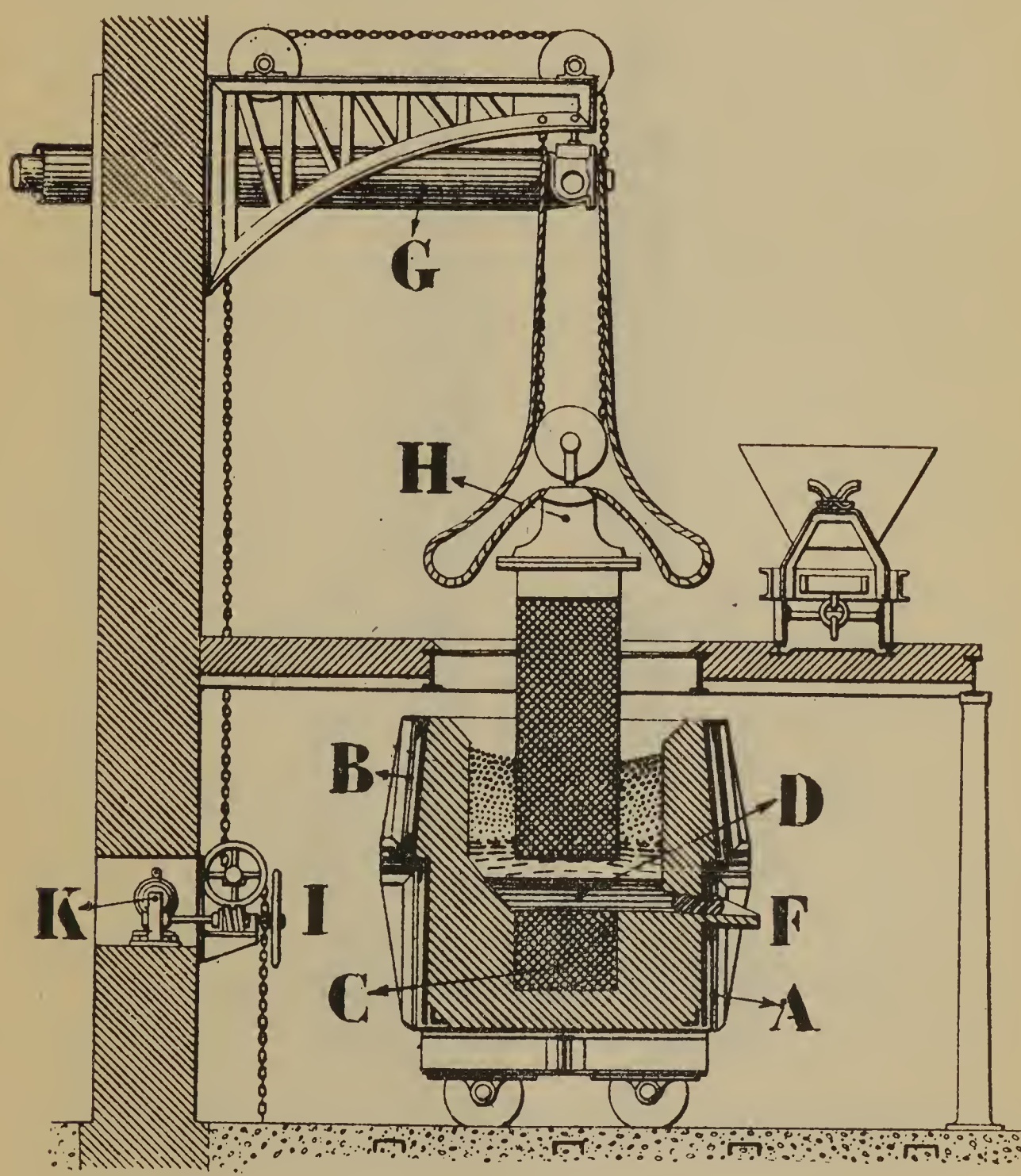

FIG. 4.

one and thence to the second movable one, in each case traversing the fused material contained in the spaces D D. The metal reduced collects in the bottom of the crucible and is cast at intervals through the tap hole F. The distance between the

movable electrodes is sufficiently great to cause the current, entirely or for the larger part, to pass through the intermediate electrode, and not to jump from one movable electrode to the other through the bath. This question of the distance apart of the movable electrodes is of prime importance, for if the

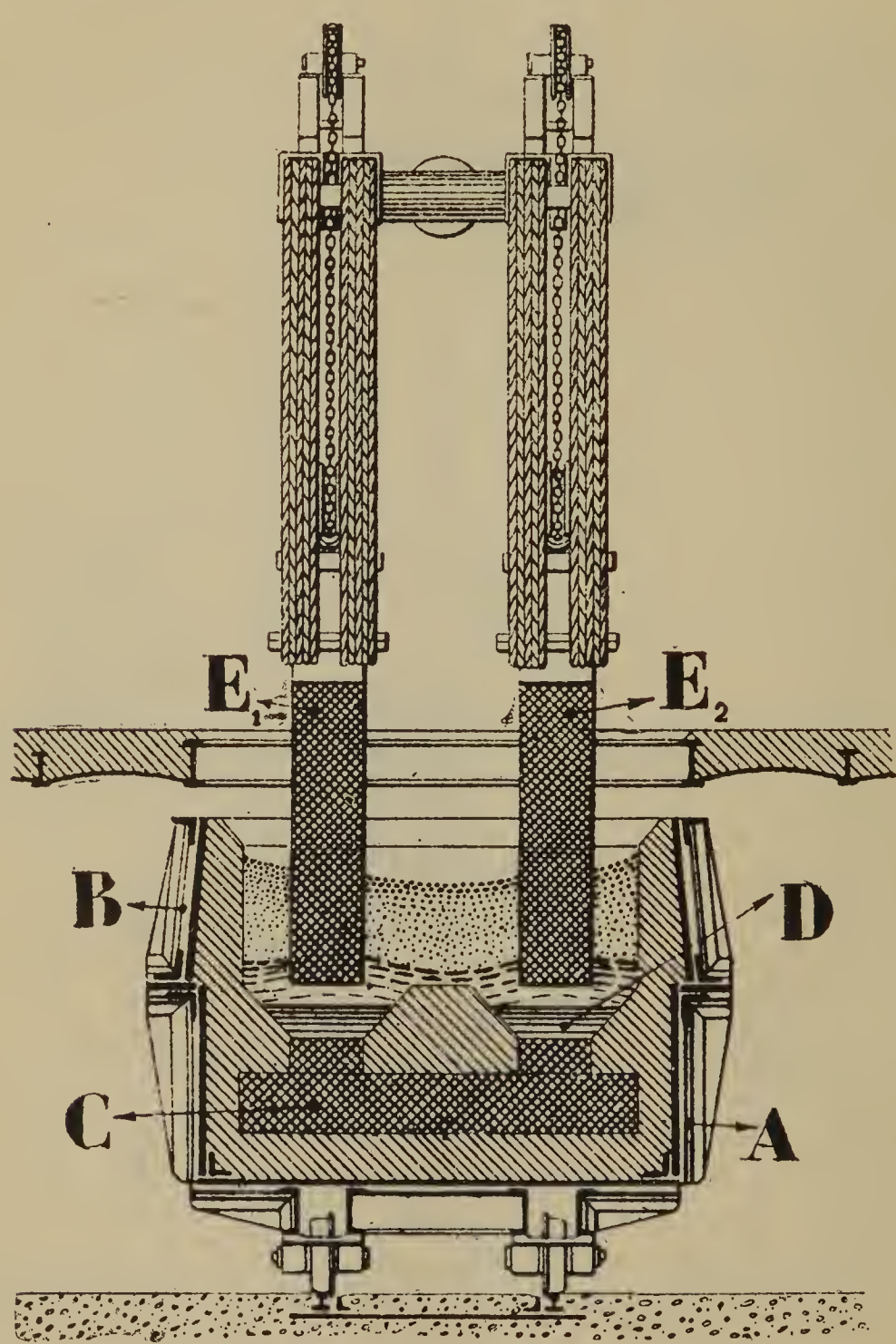

Fig. 5.

current could pass directly through the bath between the two electrodes, the bath could not be kept in place, and the crucible might even become filled up. This little inconvenience would be produced when the bath became less resistant, either by the

modification of its composition or by reason of an elevation of temperature; the controller of the furnace would then raise the electrodes, to reduce their active surface and increase the resistance of the furnace. If the current has short-circuited from one movable electrode to the other, the raising of the electrodes will be followed by a raising of the active zone of the furnace, until the furnace is running in an entirely abnormal manner with the electrodes only in the top of the crucible.

Flexible cables connect the heads of the electrodes H with the concentric conductors G. The heads of the electrodes are of bronze cast directly upon the carbons, and are hollow for the passage of cooling water. This idea of casting bronze directly upon the carbon, to make the electrical connection, is the most perfect system of connection which I have used, and was patented by me in 1900.

The raising and lowering of the electrodes is by means of the hand wheel or by the electric motor K through a worm gearing. One man regulating the electrodes K can watch over several of these furnaces in operation.

The lining of the furnace is made of refractory material, such as alumina, burnt dolomite, silica, bauxite, or chromite, that one being chosen which will be least attacked by the materials being treated. The lining material is coarsely broken, so as to obtain a certain amount of powdered material with the granules not larger than 5 mm. The mixture is heated with 7-8 per cent. of pitch intimately mixed and is tamped strongly into crucibles, using wooden forms to determine the interior shape. To produce alloys low in carbon, the intermediate electrode cannot be of carbon, since it remains in permanent contact with the metallic bath; in this case, the place of the electrode is taken by metal the same as is being manufactured in the furnace.

In the furnace just described, I put molybdenum dioxide, obtained by the calcination of ammonium molybdate, mixed with carbon, in the following proportions:

$$MoO_2 + 2C = Mo + 2CO.$$

Reduction takes place easily and there is formed a metallic bath covered with slag, on the surface of which floats carbon, the slag containing an excess of unreduced oxide. On adding

fresh materials, reduction of the oxide takes place in the upper layers, producing metal more or less carbonized, but becoming decarbonized on passing through the oxide zone of slag. I thus obtain "cast" molybdenum with not more than 2-3 per cent. carbon, using broken and tamped-in molybdenum metal in place of the intermediate electrode. After the first cast, this channel remains always full of "cast" molybdenum and continues to act as an intermediate electrode. The electric energy most suitable I find to be 140-160 watts per square centimeter of cross-section of electrodes. The furnace works well at 60 volts.

A similar furnace, with fixed carbon for intermediate electrode, works well for the Guichard process, but the voltage must be dropped to 40 because of the smaller resistivity of the sulphide, and the energy kept at 140-160 watts per square centimeter cross-section of the electrodes.

I have modified Guichard's process in such a way as to give a more resistant bath by adding lime and carbon to the molybdenite in the proportions necessary for the equation,

$$MoS_2 + 2CaO + 2C = Mo + 2CaS + 2CO.$$

Desulphurization is complete and the reaction easily controlled.

"Cast" molybdenum is very fluid, casts easily, gives in the air vivid sparks and thick fumes of molybdic acid floating around as white threads of extreme tenuity.

The oxidation of the metal and the loss resulting may be avoided by having the tap hole connected directly with the ingot mould and covering the flowing metal with a semi-cylindrical piece of refractory material.

Variation of above method.—If pure oxide and sulphide have been prepared, they may be heated in an electric furnace, mixed in the proportions required for the reaction,

$$2MoO_2 + MoS_2 = 3Mo + 2SO_2.$$

This reaction requires no sulphur, but the cast metal made always contains some sulphur and the reaction is incomplete.

Second variation.—Molybdate of magnesium may be heated directly in the same electric furnace; the molybdate is first calcined at redness with a calculated proportion of kaolin, which is simultaneously dehydrated and then enough carbon added to realize in the furnace the following reaction:

$$4MgMoO_4 + Al_2Si_2O_7 + 14C = \underbrace{Al_2Si_2O_7.4MgO}_{\text{Basic slag}} + 2Mo_2C + 12CO.$$

The kaolin is introduced to form a fusible slag, which must be basic, to avoid reduction of silica and the formation of silicides. The kaolin may be replaced by bauxite forming an aluminate of magnesia slag which is not reducible by carbon and is sufficiently fusible to be run out of the furnace. If it is desired to avoid the presence of silica altogether, ferruginous bauxite must be used containing little silica, but in this case iron is reduced into the molybdenum, forming the carburized alloy called ferro-molybdenum. This is usually no inconvenience, for molybdenum is sold almost entirely in the form of ferro-alloy.

Refining of Cast Molybdenum.

Moissan showed that "cast" molybdenum heated in contact with molybdenum dioxide lining is refined, losing its carbon. This reaction can be utilized on a large scale and produces metal containing only 0.3-0.4 per cent. of carbon. The refining of "cast" molybdenum containing no iron, however, presents difficulties because of the difficult fusibility of the molybdenum, requiring for its fusion a temperature so high that the lining of the furnace becomes pasty. Even the melting of "cast" molybdenum in the refining furnace requires the exclusion of air and the use of a very fluid slag composed of silicates, to protect the metal from oxidation. When the bath is formed and raised to a sufficiently high temperature, molybdenum dioxide, or the blue oxide, is thrown on the surface and rapidly oxidizes the carbon of the "cast" metal. Considerable molybdic acid is volatilized in the operation, which may be partially collected in a sublimation chamber as a felty mass of white, brilliant crystals.

The "cast" molybdenum can likewise be melted in a resistance furnace under a bath of fused alumina (bauxite free from iron and silica by a previous fusion in the electric furnace with a proper proportion of carbon—Hall process). Molybdate of calcium is then thrown into this slag, which acts as a reducing

agent upon the carbon, its molybdenum passing into the bath and its lime into the slag, while the carbon is thereby oxidized.

Refining with Flowing Electrodes.

"Cast" molybdenum may be refined by the use of flowing electrodes, such as I devised in 1897. The electrodes, instead of being of carbon, as in the ordinary furnace, are formed of "cast" molybdenum, containing not over 3 per cent. of carbon; higher carbon metal is too brittle, cleaving easily into small crystalline prisms. The furnace used is like that described, with two hearths in series, the intermediate electrode being the bath of metal. On starting the operation, this intermediate electrode is made of fragments of molybdenum broken up and tamped in. The lining of the crucible is burnt dolomite agglomerated with pitch.

The preparation of the intermediate electrode may be simplified by putting in the hearth of the furnace, in a canal cut out for it, a long ingot of molybdenum, the extreme ends of which reach to the two electrodes, so as to close the circuit. The ingot of molybdenum is rapidly melted down by the current. It is covered with molybdenum dioxide, pure alumina is added, and when a slag is formed more is added, until the electrodes touching this slag commence to melt. The drops of the melted electrodes traversing the oxidizing slag are oxidized according to the reaction,

$$2Mo_2C + MoO_2 = Mo_5 + 2CO.$$

The refining is rapid and accompanied by very small losses, for the hearth is closed and any molybdic acid vapors volatilized are caught in a condensing chamber. The current used is 140-150 watts per square centimeter of cross-section of electrodes, and the voltage, 50-60. Air must be kept out of contact with the electrodes, otherwise they will take fire where they are red-hot, producing a wasting of the electrodes just above the bath, as is shown in Fig. 5, a, and leaving no appreciable residue, for the molybdic acid formed sublimes and disappears. To avoid this destructive action on the electrodes, they should be coated with a layer of molybdenum dioxide agglomerated, with pitch pasted upon them. Successive layers of this are painted on

with a brush, powdered dioxide being sprinkled in excess on the surface, and the electrode is ready for use.

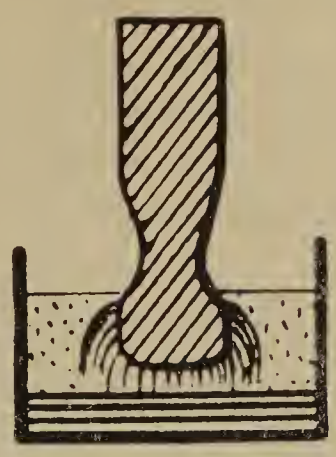

FIG. 5, a.

REFINING IN AN INDUCTION FURNACE.

Induction furnaces have been known since the patent taken out by Ferranti, in 1885. They consist of an annular crucible, with which is engaged a closed magnetic circuit carrying the primary winding, while the annular crucible forms the single secondary circuit. On passing the primary current, another current is induced in the secondary, whereby its resistance is transferred entirely into heat.

The induction furnaces at present employed have inconveniences coming directly from the phenomenon of induction, on which they are based. The annular form of the secondary circuit has a corresponding coefficient of self-induction, which increases with the dimensions of the circle. Likewise, the coefficient of mutual induction of the primary and secondary circuits increases with their distance apart, and therefore with the dimensions of the secondary circuit enveloping the primary. The size of the secondary is therefore limited by these considerations, and for powerful furnaces no practicable dimensions are compatible with high electrical efficiency. In fact, it being assumed that the size of the channel may not pass a certain limit, the capacity of the furnace can be increased only by increasing the size of the section of the channel, which diminishes its ohmic resistance, while its inductance remains almost constant. It naturally results that the proportion of the current lost increases with the power of the furnace to such a point as to render impossible the construction of a furnace of great power.

To avoid the mutual induction of the circuits and the self-induction of the secondary, the frequency of the primary current may be diminished, but as the weight of iron in the magnetic circuit varies almost inversely with the frequency, it results, in large furnaces, in inductors of enormous weight and dimensions. This lower frequency is complicated by a lower power factor, which likewise increases the cost of suitable generators.

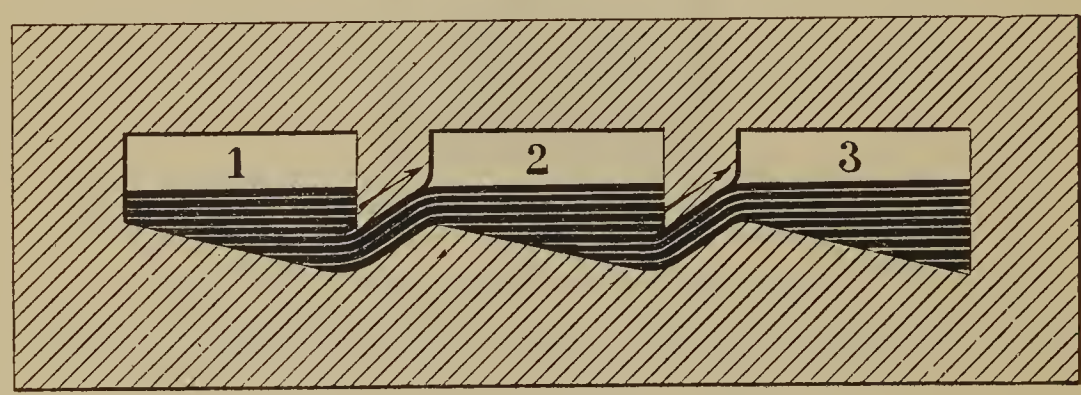

Fig. 6.

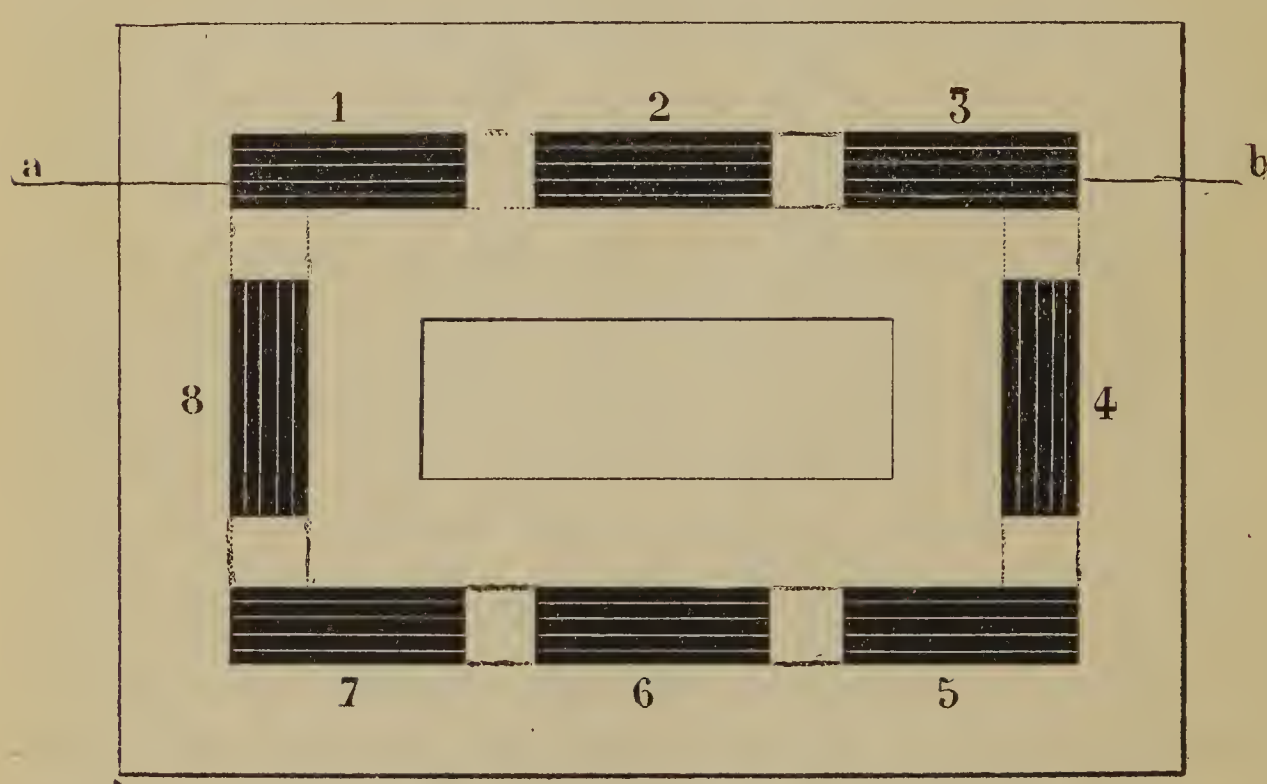

Fig. 7.

On the other hand, in the usual type of induction furnace it is difficult to obtain uniform heating and distribution of the reaction, because of the small heat conductibility and the slight diffusion of the melted material. The technical effect is certainly much better when there is continuous circulation of the melted materials, so as to mix the liquid and solid materials with each

other. I have obtained this circulation by having the crucible or secondary in the form of a series of channels, the bottom of which is inclined in a longitudinal direction, with smaller channels connecting the deeper parts of each channel with the shallower parts of the next succeeding one, the Joule effect being inversely as the sections of the channels are greater in the constricted parts than in the deep parts of the channels, producing a difference of density in the channels resulting in an ascensional movement and continuous circulation in one direction throughout the series of canals.

Figs. 6 and 7 show a rectangular form of the crucible, with eight distinct canals, shown in vertical section in Fig. 6, in plan in Fig. 7. Figs. 8 and 9 show variations having circular and oval forms of crucibles. A large number of similar variations

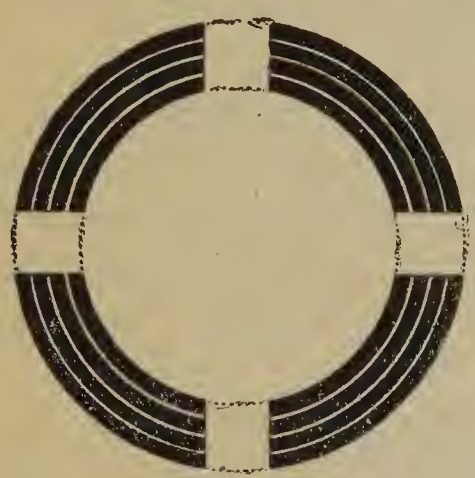

Fig. 8.

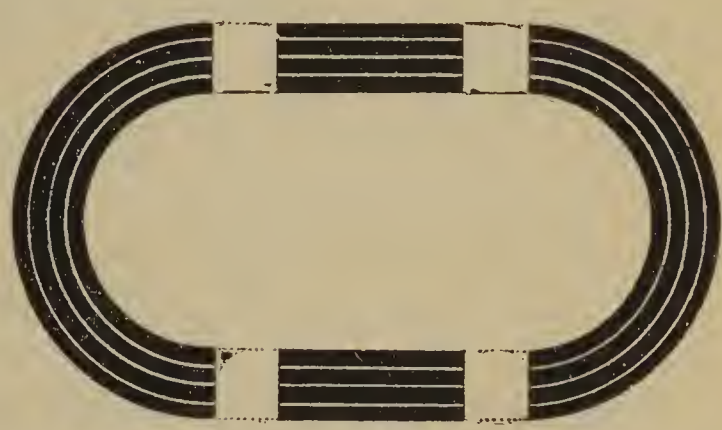

Fig. 9.

of the same may be readily conceived. My arrangement has nothing in common with the combination of conduits and uncovered basins which have been patented by others. For instance, in the Schneider furnace, the heating by the induced current is localized in tubes of small cross-section and high resistance, enclosed by the magnetic induction circuit. This system is exterior to the furnace proper. The circulation of the molten metal is limited to these exterior tubes, and is communicated to the basin in the hearth of the furnace only by circulation to and from it. The mass of the molten metal cannot participate actively in this circulation, and thus uniform heating is impossible to obtain on this principle. Using the arrangement which I have proposed, a single inductor suffices for the whole circuit, which is entirely in the circulatory system.

My furnace produces an industrial effect more complete and perfect and of considerable importance to the manufacture of metals having a high fusing point, like molybdenum, tungsten, uranium and their alloys. It may also be used for the manufacture of steel by the direct fusion of chosen materials or for the refining of impure metals.

Figs. 10, 11, 12 and 13 are sections of this furnace. Photographs 14 and 15 and Figs. 16, 17, 18 and 19 are exterior views.

The furnace consists of a sheet-iron box containing the whole electric and magnetic systems, and rests on two trunnions f. The channels a, with free surface and called the working channels, are placed parallel to each other and inclined longitudinally, and are connected at their ends to conduits with circular sections b, called the heating conduits, which connect the deeper end of each channel with the more shallow end of the following one.

The primary circuit consists of a copper coil placed around the upper horizontal branches of the double magnetic circuit cc. The two coils d constitute the primary and have the same number of turns, and are connected in series. The secondary circuit is constituted of the conducting material in the channels a and the conduits b.

Metallic chambers e, traversed by a current of water, are placed between the internal faces of the magnetic circuit and the channel masonry, in order to afford as complete cooling as possible, as likewise to protect the inductor cables against radiation of the heated masonry.

The masonry is not placed in direct contact with the lateral faces of the inductor, but is separated from it by ribbed plates. The cooling air passes between the plates and the inductor.

An external fan sends a current of air, which is divided between the magnetic fields and the primary coils, so as to continuously cool the primary circuit and the fields of the inductor. The air enters by the hollow trunnions f and wind boxes g. Dampers moved by chains, pulleys and an endless screw permit the regulation of the air circulation so as to properly divide it.

The lining of the furnace rests in a box of magnesia bricks and consists of crushed dolomite agglomerated with pitch, like the hearths of open-hearth furnaces. The walls of the closed

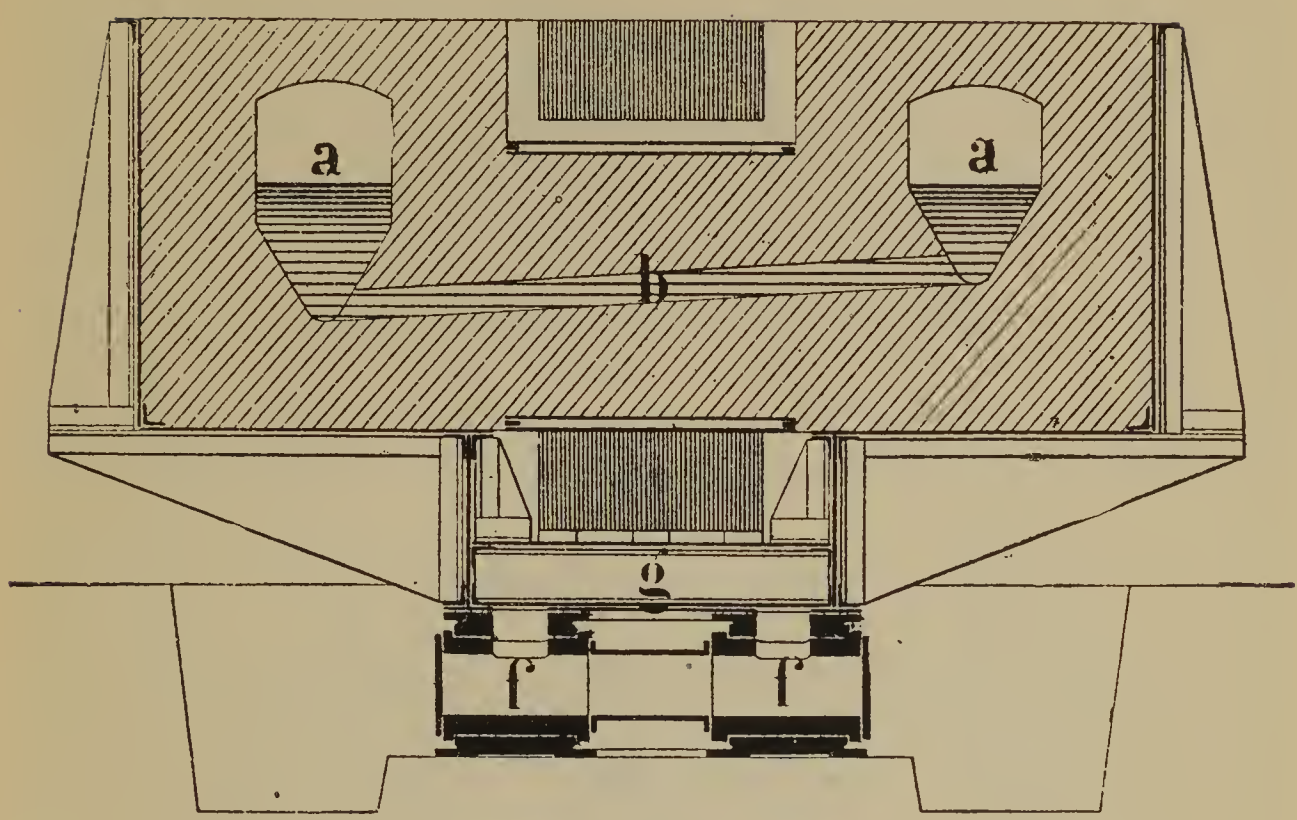

Fig. 10.

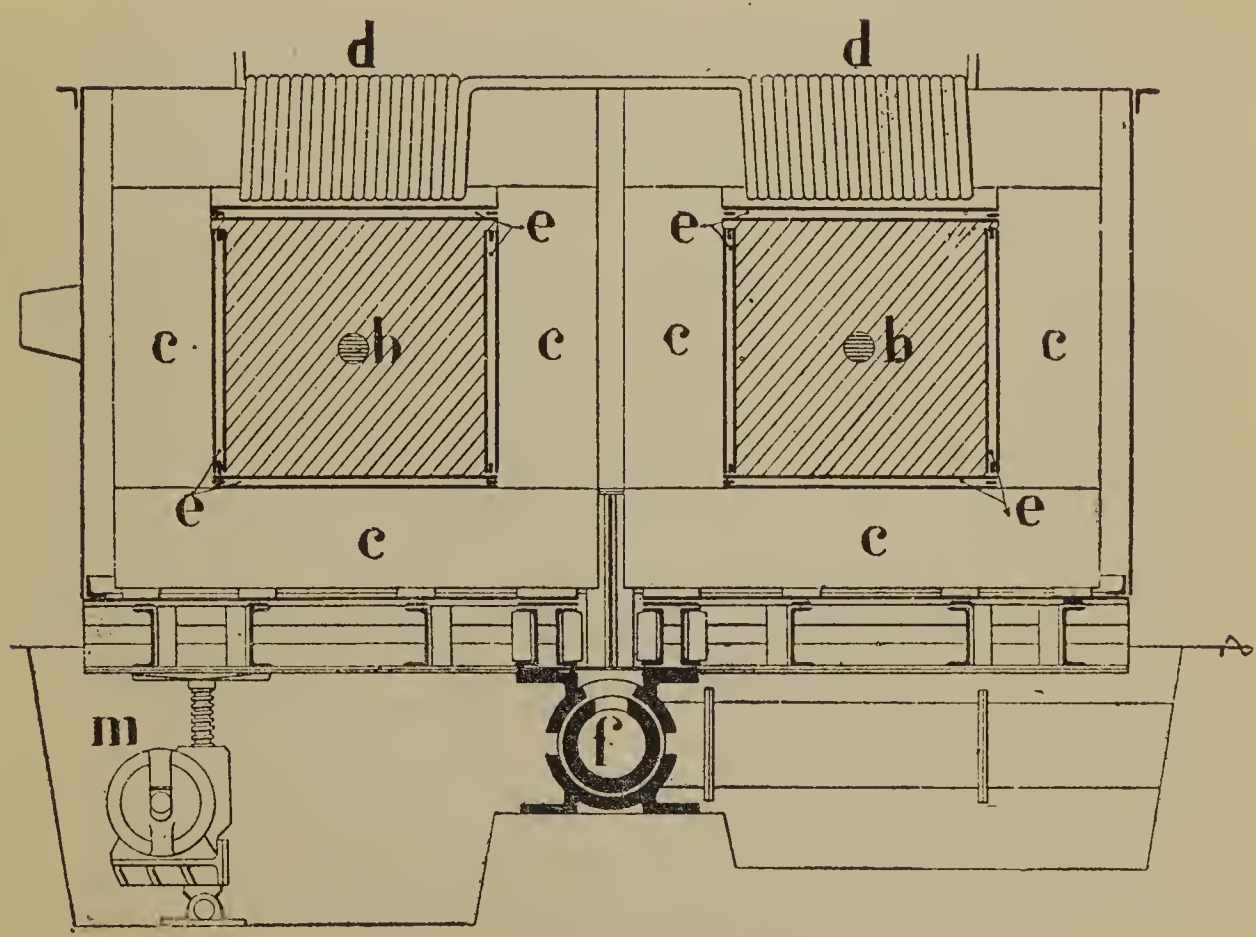

Fig. 11.

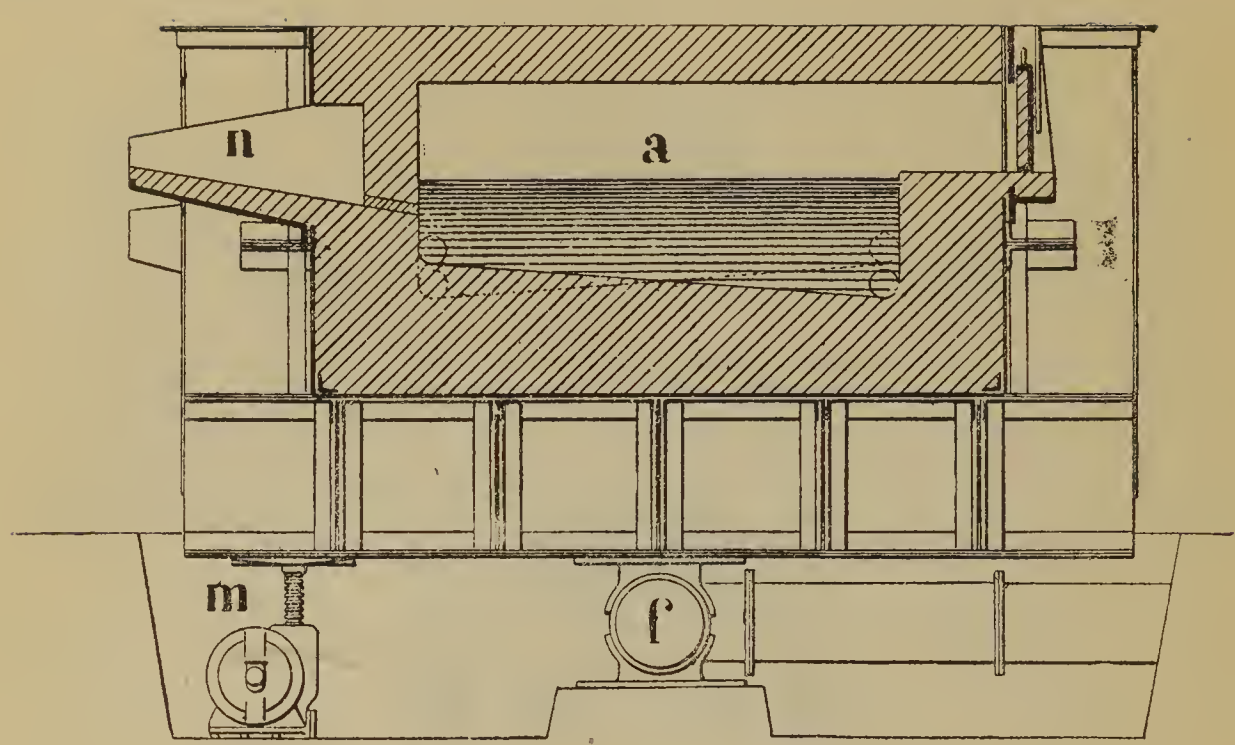

FIG. 12.

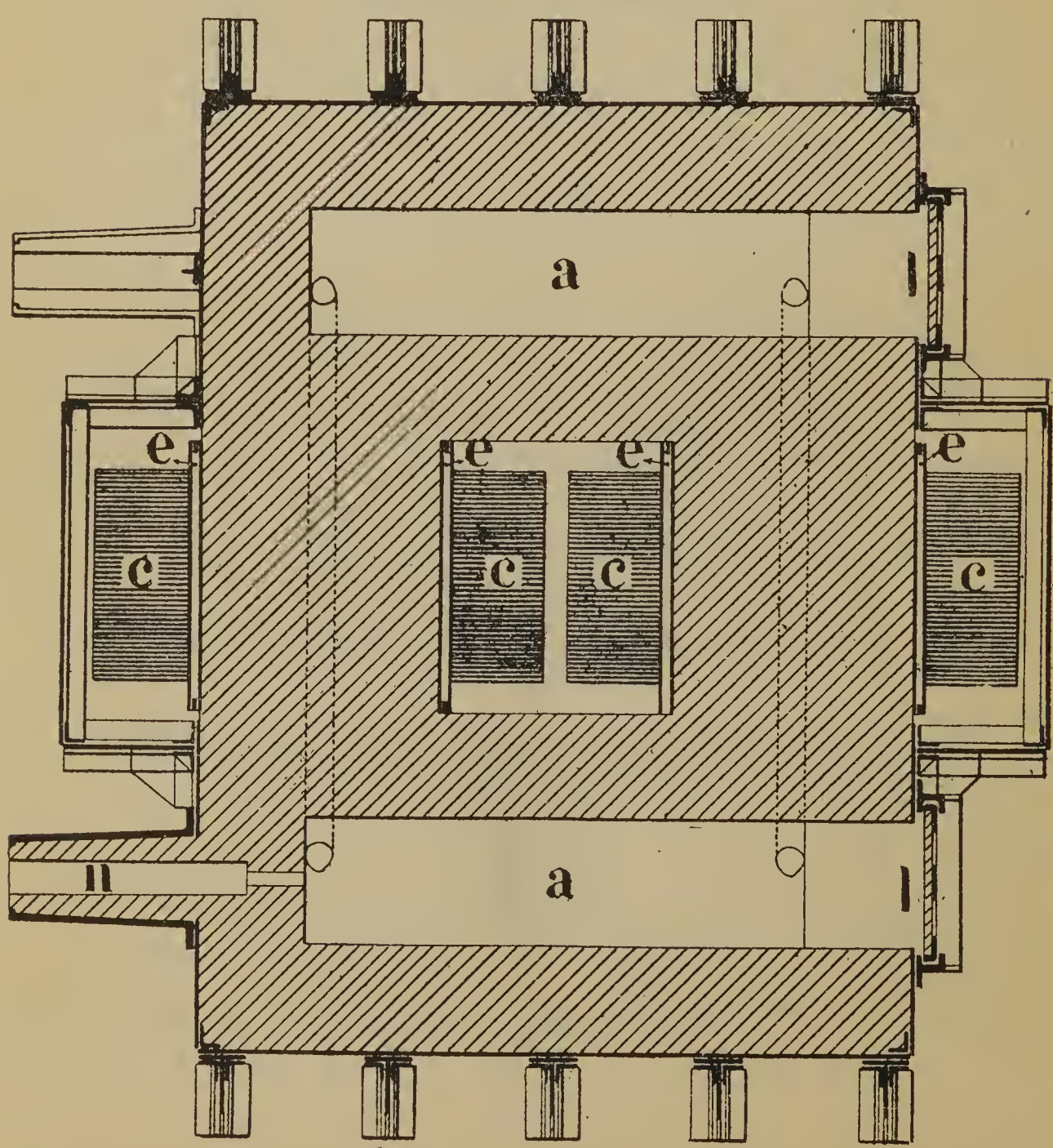

FIG. 13.

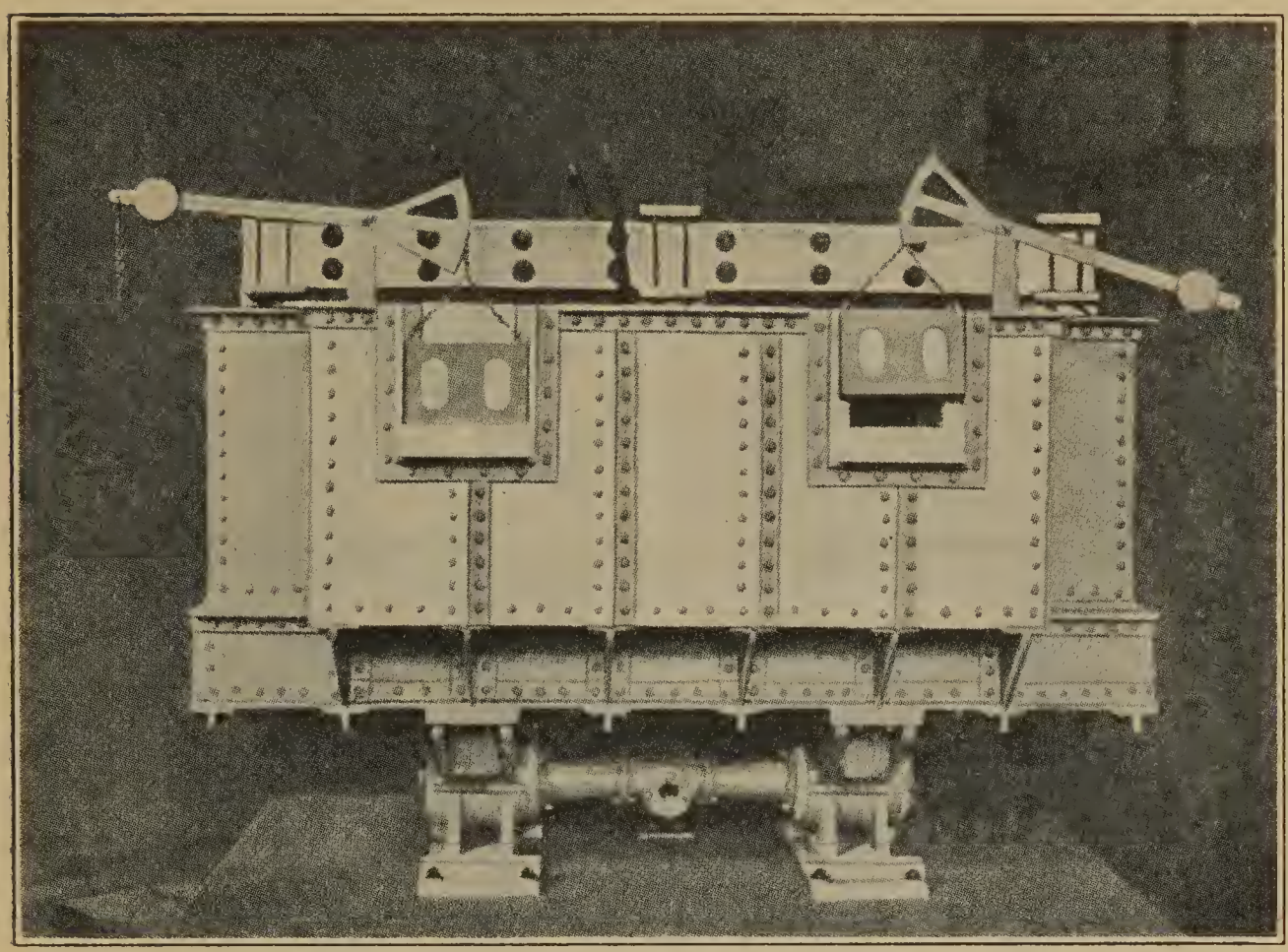

FIG. 14.

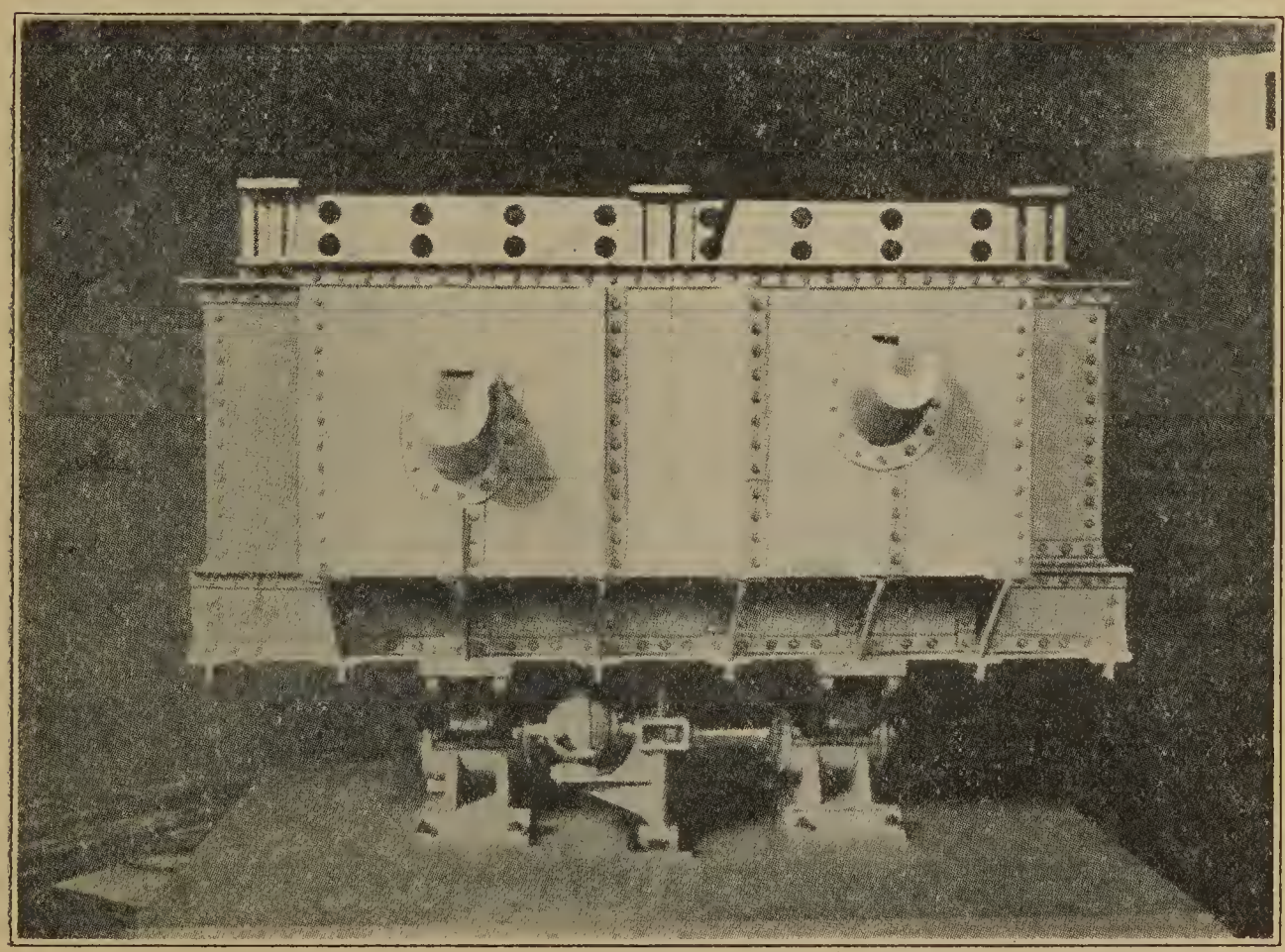

FIG. 15.

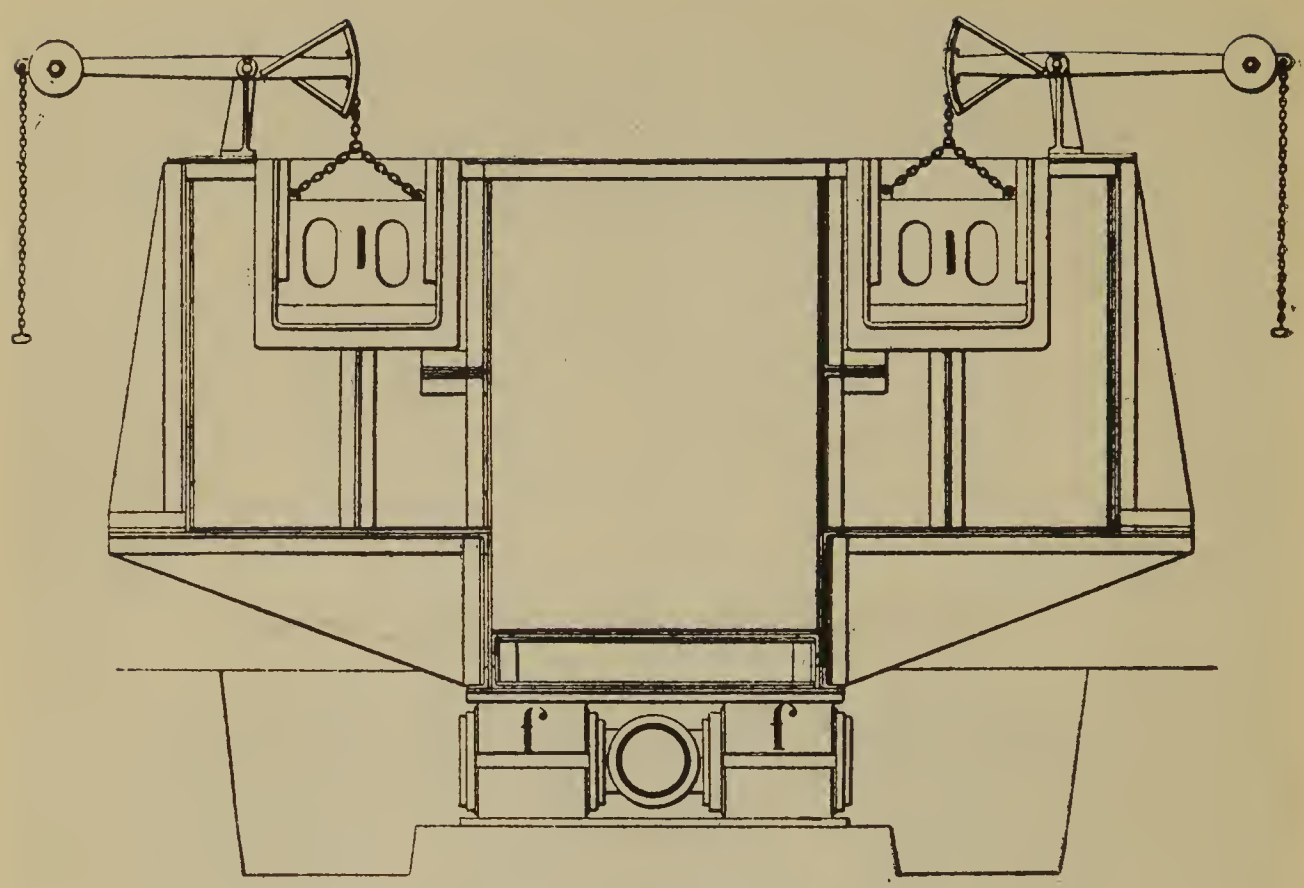

FIG. 16.

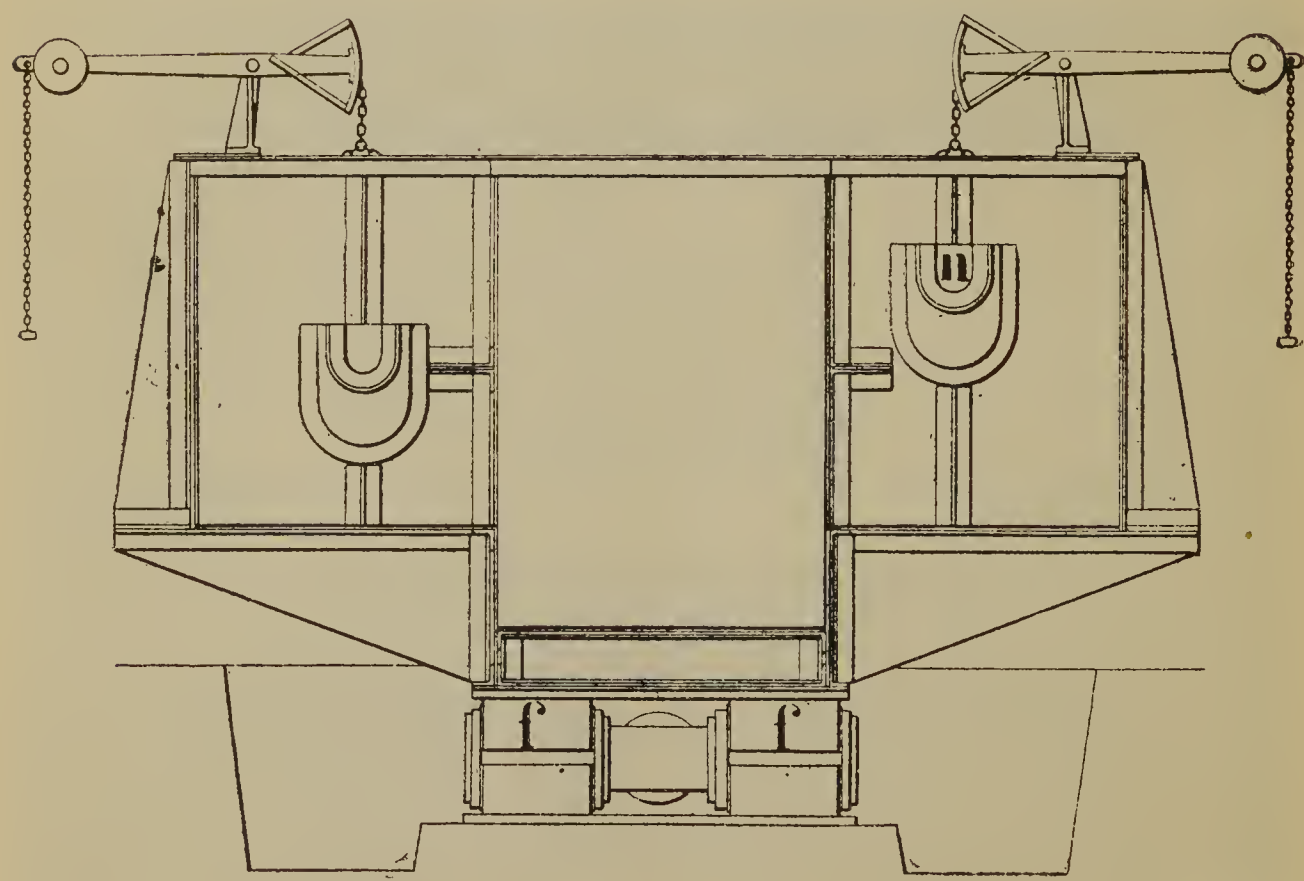

FIG. 17.

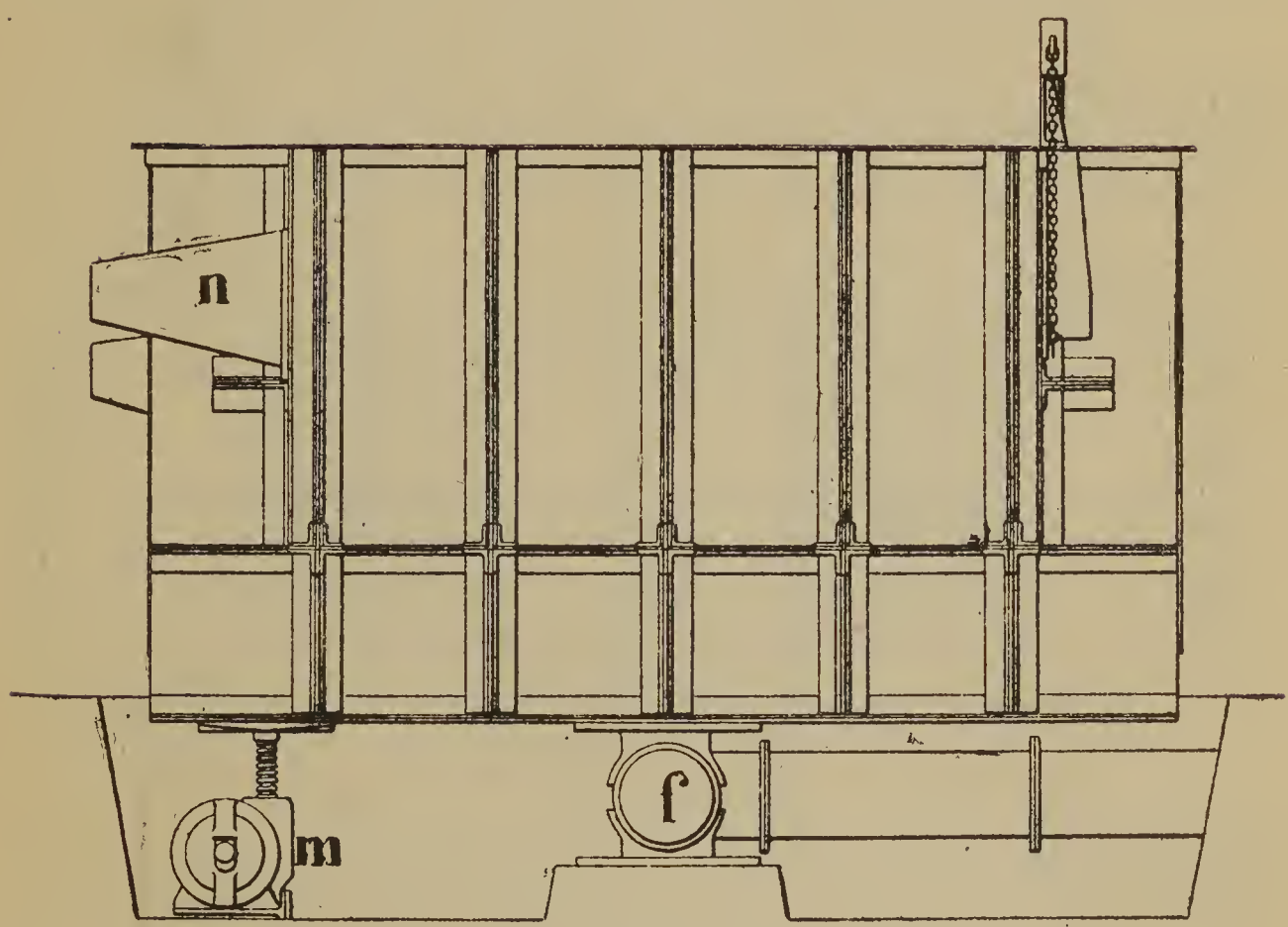

FIG. 18.

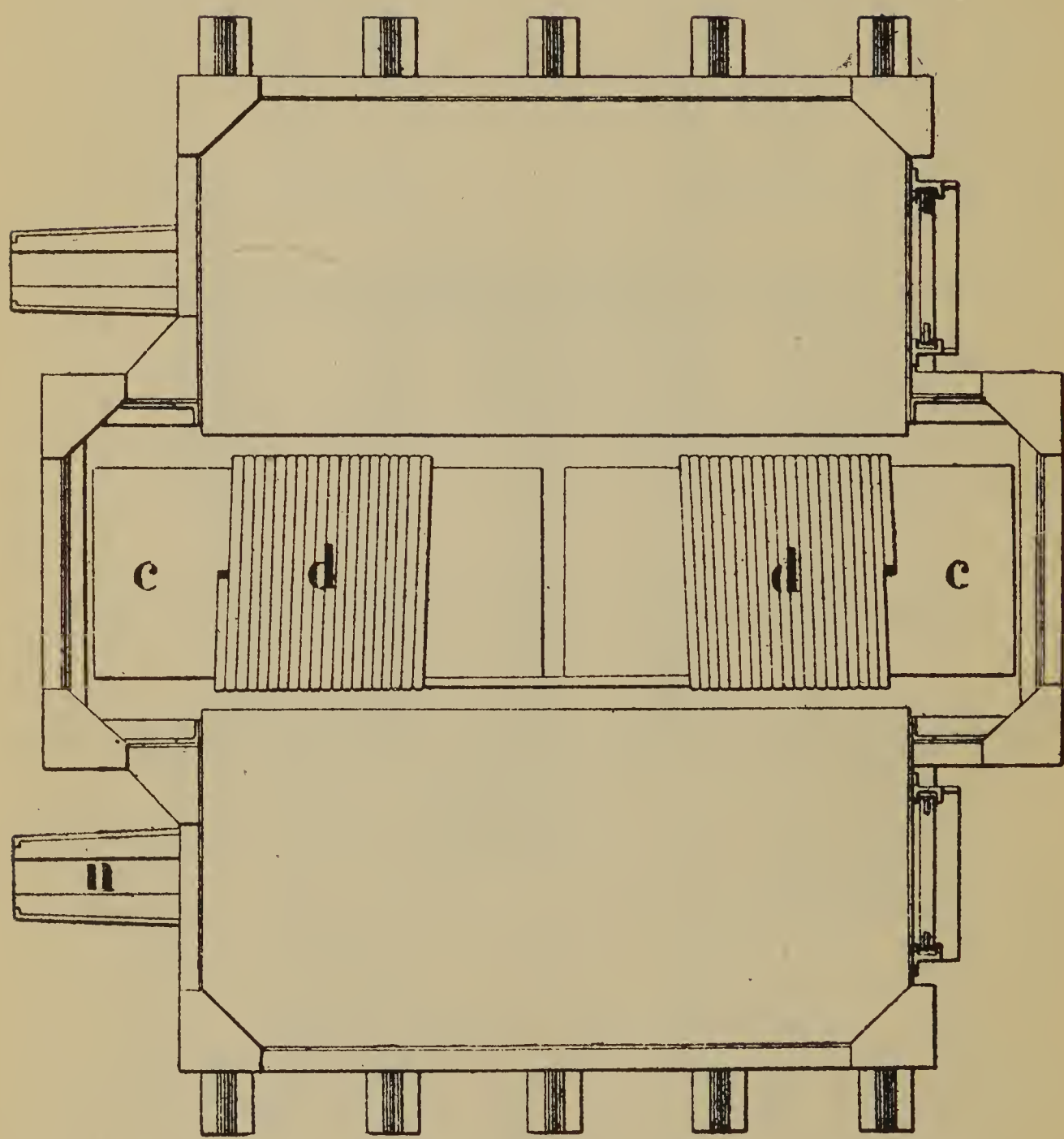

FIG. 19.

conduits are of pure magnesia, to avoid corrosion by the silicon and the carbon in the "cast" molybdenum being refined.

On starting, the masonry is baked by a gas flame, furnished by some sort of a gas oven, and liquid metal is run into the channels until it completely fills the closed conduits. In all of the operations, after casting, this same quantity of metal is kept in the channels, so as to prevent slag from entering them and the closed conduits, and thus avoiding any breaking of the current. Materials are charged and the furnace worked through the doors l.

The trunnions f and the electric-driven jack-screw m allow of the running out of part or all of the slag, without interrupting the passage of current. The metal can be likewise cast through the tap hole.

As much metal may be cast as one wishes and as often as one desires, for the heating need never be interrupted, even during casting.

Induction Circulation Furnace for Reduction.

The furnace which I have just described may also be used for the reduction of molybdenum dioxide. In this case, the Joule effect is also effected in the liquid metal constituting the secondary circuit, to which is now given a T-shaped section, in order to obtain good electrical conduction and large contact surface with the material to be reduced. The ore is mixed with pulverized coke and placed upon the surface of the metallic bath through doors at each end of each channel. The two channels are united by a hood connecting all metallic conduits with a chimney or with a condensing apparatus, if it is necessary to condense any metallic vapors. Thus used, the induction furnace may produce ferro-molybdenum with a low carbon content, or my process for reacting between oxides and sulphides may be employed. I will return to this method further on.

Manufacture of Molybdenum Silicide.

I prefer to use for the manufacture of molybdenum silicide my furnace with two hearths in series. The mixture to be reduced should contain a considerable excess of silica above that

theoretically necessary, as represented in the silicon of the product to be obtained. For instance, to produce the silicide Mo_2Si_3, theory would indicate to use 180 parts of silica to 256 parts of molybdenum dioxide, according to the reaction

$$2MoO_2 + 3SiO_2 + 10C = Mo_2Si_3 + 10CO.$$

In practice, however, it is necessary to use at least two and one-half times as much silica as molybdenum dioxide. In a furnace with carbon electrodes, it is necessary to use an energy density of 130-140 watts per square centimeter of cross-section of electrodes.

Silico-Thermic Manufacture of Molydenum and Ferro-Molybdenum with Low Carbon Content.

This may be done in an electric furnace using carbon electrodes and hearths in series, or it is preferable to use either an electric furnace with flowing electrodes or an induction furnace. It is also possible to obtain molybdenum with low carbon content by reacting between the silicide of molybdenum and the dioxide, and to obtain ferro-molybdenum by the reaction of ferro-silicon on molybdenum dioxide, in which case the silicide may be made in a refining furnace, where, after running off the slag, the operation may be continued by throwing upon the surface of the bath a mixture of molybdenum dioxide and lime.

Application of the above processes, starting from impure molybdenite.—It may be interesting to calculate the cost of porducing a ton of ferro-molybdenum, starting from an impure ore.

Let us take a molybdenite having the following composition:

MoS_2	56.21	per cent.
SiO_2	29.21	" "
Al_2O_3	3.00	" "
P_2O_5	0.73	" "
Cu_2S	1.58	" "
PbS	4.86	" "
CaO	2.29	" "
Miscellaneous and loss	2.09	" "

To make the calculation more convenient, the composition of a

ton of this material may be expressed in the number of kilogram molecules which it contains. For instance, the above analysis is represented by the formula,

$$3.5MoS_2 + 5SiO_2 + 0.3Al_2O_3 + 0.05P_2O_5 + 0.1Cu_2S + 0.2PbS + 0.4CaO.$$

Supposing, that one uses to manufacture the molybdenum dioxide the simplified method previously described, consisting in roasting, and the ammoniacal solution of the roasted residue, followed by a precipitation of the phosphoric acid as ammonio-magnesium phosphate and the molybdate of ammonia being calcined for molybdenum dioxide.

Scheme of operations.—The material, after roasting, will have become

$$3.5MoO_3 + 5SiO_2 + 0.3Al_2O_3 + 0.05Ca_3P_2O_5 + 0.2CuO + 0.2PbO + 0.25CaO.$$

After digestion with ammonia, followed by concentration by evaporation, crystals of the molybdate will be formed of the composition

$$\tfrac{1}{2}(7MoO_3.NH_4O.4H_2O)$$

The small quantity of phosphoric acid carried along is precipitated by magnesium chloride. These crystals are calcined to get MoO_2 and the regeneration of a large part of the ammonia. If the operations are continued with care, the loss of ammonia will not exceed 60-65 kilograms of commercial ammonia per ton of ore treated.

Practical data.

In practice, it may be assumed that the operation will require per ton of ore treated:

Ammonia	65	kilograms
Chloride of magnesium	10	"
Coal	1,000	"

The treatment of a ton of ore with 56 per cent. of molybdenite will furnish 430 kilograms of molybdenum dioxide.

The electric reduction of carburized molybdenum and refining thereof will require per ton of 80 per cent. ferro-molybdenum

Electrical energy	6,000	kilowatt-hours
Electrodes	90	kilograms
Carbon for reduction	300	"

Direct reduction of the dioxide for 80 per cent. ferro-molybdenum will require

Molybdenum dioxide	1,050 kilograms
Ore containing 56 per cent. MoS_2	2,450 "
Ferro-silicon of 53 per cent. silicon content	450 "
Electrical energy	1,000 kilowatt-hours

Cost of Producing a Ton of 80 per cent. Ferro-Molybdenum by the Molybdenum Carbide Process.

I.	Raw Materials—		
	Molybdenum ore, 56% molybdenum sulphide, 2,450 Kg @ $7 per unit of MoS_2, 2.45 × 7 × 56 =	$960 40	
	Ammonia, 200 Kg @ $8.00 per 100	16 00	
	Scrap iron, 225 Kg @ $14.00 per ton	3 20	
	Magnesium chloride and miscellaneous	8 40	
	Total		$ 988 00
II.	Electrodes and Fuel—		
	Coal for preparation of MoO_2, 2,500 Kg @ $5.20 per ton	$13 00	
	Coke for electrolytic reduction, 300 Kg @ $8.00 per ton	2 40	
	Carbon electrodes, 90 Kg. @ $8.00 per 100 Kg	7 20	
	Total		$20 60
III.	Electric Energy— 6,000 kw-h @ 0.24c		$ 14 40
IV.	Labor		6 00
V.	Repairs and maintenance		5 00
VI.	Sinking fund		12 00
VII.	Interest on ore and products in stock		16 00
VIII.	General expenses, unforeseen, miscellaneous		36 00
	Total		$1,100 00

Cost of Producing a Ton of 80 per cent. Ferro-Molybdenum, Using 53 per cent. Ferro-Silicon for Refining.

I.	Raw Materials—		
	Molybdenite of 56% MoS_2 content, 2,450 Kg @ $7.00 per unit of MoS_2, 2.45 × 7 × 56 =	$960 40	
	Ammonia, 200 Kg @ $8.00 per 100 Kg	16 00	
	Scrap Iron, 225 Kg @ $14.40 per ton	3 20	
	Magnesium chloride and miscellaneous	8 40	
	Total		$988 00
II.	Ferro-Silicon, 53% silicon— 450 Kg @ $80.00 per ton		36 00
III.	Electric energy— 1,000 kw-h @ 0.24c		2 40
IV.	Labor		5 00
V.	Repairs and maintenance		5 00
VI.	Sinking fund		12 00

VII.	Interest on ore and products in stock	16 00
VIII.	General expenses, unforeseen, miscellaneous	37 60
	Total	$1,100 00

The cost prices are therefore alike for the two processes. But there is an advantage in using that process which can use the least pure material, the cost of which is considerably lower than the richer material. The comparison is still more interesting if the silico-thermic process is compared with the alumino-thermic. In fact, the production of a kilogram of 80 per cent. ferro-molybdenum requires in practice 420-450 grams of aluminium at a cost for aluminium of $200-$240 per ton of ferro-molybdenum.

If the ferro-molybdenum can be sold for $2.50 per kilogram of contained molybdenum, or at about $2,000 per ton, the profit figures out $900, a very satisfactory figure if it was not for the perpetual uncertainty of the market and the variation in the selling price. It would certainly be better to make less profit per unit and to sell more material. The manufacture of steel will absorb easily and voluntarily a considerable quantity of ferro-molybdenum and molybdenum if the price is kept at acceptable figures. The ores should be better exploited on a large scale, creating a stable market and a steady foundation for the industry.

In the assumptions made, considerable allowances have been made for general costs and accessory expenses, such as would inevitably be met with in the production on a small scale of ferro-molybdenum. However, it would be better that this manufacture should be run as an accessory to some works, and not as the sole manufacture, so that it could be worked alongside of electro-metallurgical processes handling many tons of other materials, which would diminish very largely general costs, sinking fund, superintendence, etc. But all of these economies would not greatly reduce the price of the metal, since the cost of the ore figures as nearly 80 per cent. of the total cost.

The working cost of producing a ton of ferro-molybdenum, leaving out the cost of the ore, is about $100-$120 per ton, and may even be reduced below this in a large establishment. The actual manufacturing cost is only 12-15 cents per kilogram of contained molybdenum.

Cast molybdenum is preferable for industrial use over powdered metal, which is always more or less oxidized and causes considerable loss when incorporated into steel. It is, indeed, preferable to employ the more fusible alloys, such as ferro-molybdenum and ferro-nickel, than to use the pure molybdenum, because of its difficult fusibility.

Nickel-Molybdenum.

For certain steels, the eutectic alloy $NiMo_2$ is used, which being more easily fusible than molybdenum or ferro-molybdenum, finds preference.

It is prepared by refining molybdenum carbide by oxide of nickel in one of the special furnaces already described. The reaction is not more difficult to produce than the production of pure molybdenum or ferro-molybdenum as worked according to the reaction,

$$Mo_2C + NiO = Mo_2Ni + CO.$$

The alloy obtained contains 75-76 per cent. of molybdenum and 22-23 per cent. of nickel. The method of operation of the process is absolutely the same as that described for the refining of carbonized molybdenum by molybdenum dioxide.

As I have previously explained, the silico-thermic method may be used, reacting on the silicide of nickel by molybdenum dioxide or reciprocally on molybdenum silicide by nickel oxide, working exactly in the same manner as for simple refining.

$$NiSi + MoO_2 + CaO = CaSiO_3 + MoNi.$$
$$Ni_2Si + MoO_2 + CaO = CaSiO_3 + MoNi^2.$$
$$Mo_2Si^3 + 6NiO + 3CaO + 3CaSiO_3 = 2MoNi_3.$$

These examples show how very interesting is the electro-metallurgy of these alloys. Nickel-molybdenum up to 75 per cent. of molybdenum may be thus obtained. The use of such an alloy increases the ductility of hard steels and gives them greater elongation, allowing of its use for large forged pieces. They are used also in the proportion of 0.5-1.0 per cent. in hard chrome steels for armor plates and shells, permitting such alloys to be worked with ordinary machine tools.

Chrome Molybdenum.

This alloy is obtained by refining in one of my electric furnaces chromium silicide by chromium dioxide, with the addition of lime according to the reaction,

$$SiCr_2 + MoO_2 + CaO = CaSiO_3 + MoCr_2.$$
$$SiCr + MoO_2 + CaO = CaSiO_3 + MoCr.$$

The reaction is never complete and the slag contains molybdenum which must be recovered. The alloys contain 35-53 per cent. of chromium and always retain a little silicon, the presence of which is not injurious.

The Action of Molybdenum in Steels.

Molybdenum increases largely the ductility and elasticity of hard steels, for 0.25 per cent. of molybdenum will increase the extension to the point of rupture 40 per cent. Molybdenum alloyed with nickel is very useful for rifle and cannon steels and for boiler plates for high pressures. Molybdenum is used also in rapid-cutting tool steels in the proportions of 0.5-10 per cent.

Metallography.

L. Guillet communicated to the Metallurgical Congress at Liege, July, 1905, the following: Steels containing 0.2 per cent. carbon and 0.2-1.0 per cent. of molybdenum contained perlite more clearly visible than in ordinary steels. Above 2 per cent. molybdenum the structure changes and the perlite becomes extremely finely divided; it disappears when the steel contains 5 per cent. of molybdenum, being replaced by a special constituent characterized by a thin, fine net-work.

In the series of steels with 0.8 per cent. of carbon, there is at first finely-divided perlite. When 1.2 per cent. of molybdenum is present, there are visible small, white, isolated grains of a special constituent which increases as the molybdenum is increased. At 10 per cent. there is to be seen around these white kidney-shaped patches a true eutectic, apparently formed by iron and the special constituent.

The following table contains the result of the metallographic investigation:

Microstructure	Steels with 0.2% Carbon	Steels with 0.8% Carbon
Perlite	0-2% Molybdenum	0-1% Molybdenum
Special Constituent	Molybdenum > 2%.	Molybdenum > 1%

Properties.

The perlitic steels have a tensile strength much higher than ordinary steels, but in spite of that gave great elongation and high reduction of area. They are not more brittle, but sensibly harder than the carbon steels. The steels containing the special constituent (double carbide of molybdenum and iron) have a tensile strength and elastic limit extremely high, but a small elongation and reduction of area. They are very brittle and very hard.

In summating, molybdenum gives the same results as tungsten, but only one-quarter as much is required.

Uses.

The molybdenum steels are used for tool steels, but have been kept rather in the background by the tungsten steels, which are cheaper. It has been proposed and tried to use steels containing up to 0.25 per cent. of molybdenum, with variable proportions of nickel, for the manufacture of very strong steel wire, boiler plates, cannons and guns. These steels are especially adapted for high pressure boilers used on naval vessels.

The addition of 1 per cent. of molybdenum to chrome steels of great hardness permits of their being worked rather easily, a fact of great importance in the manufacture of armor plates and projectiles.

It is certain that the consumption of molybdenum would be very much greater if the price was lower.

Moissan[4] has proposed using molybdenum as a deoxidizing agent in the metallurgy of iron.

"When into a metal saturated with oxygen, such as is obtained

[4] Le four Electrique (1897), p. 227.

in the first period of the Bessemer blow, manganese is added, it oxidizes and passes into the slag. It has been proposed to use aluminium, which gives good results, but which produces solid alumina. If molybdenum was used under the same conditions, it would have the following advantages:

"1. Furnishing a volatile oxide, molybdic acid, which would immediately escape, stirring up the whole bath.

"2. Employed in slight excess, it would leave in the bath a metal as malleable as iron, and capable of being tempered like it."

Moissan's conclusions are very judicious, but would require that molybdenum were furnished to the steel industry at a moderate price, which is not at present the case.

Analysis of Ores and Compounds of Molybdenum.

The principles of the analyses have mostly been taken from Carnot's treatise. The methods described have been tested by many chemists or else taken from reliable technical publications.

Characteristic Reactions of Molybdenum.

All molybdenum solutions become blue by the reducing action of metallic zinc, afterwards green or brown as the reaction lasts, molybdic acid being reduced in steps to the sesqui-oxide. If the liquid is brown and a little fresh molybdate is added, reduction to the blue coloration of the molybdate of the dioxide is produced. The hydrochloric acid solution of any molybdate also becomes blue by the reducing action of sulphurous acid, sugar, alcohol, tartaric acid, etc. A molybdate acidified with sulphuric acid, for example, becomes a yellow or orange color in contact with hydrogen dioxide, sodium dioxide, or barium dioxide. Molybdate of ammonia or potassium solution acidified with nitric acid gives a yellow precipitate of phosphomolybdate of ammonia or potassium on the addition of a little phosphate solution, such as that of sodium. A current of hydrosulphuric acid, or the addition of an alkaline sulphide, to an alkaline molybdate solution forms a soluble sulpho-molybdate of a ruby red color, decomposed by hydrochloric acid, giving a reddish-brown precipitate of hydrated trisulphide of molybdenum.

Blowpipe Tests.

Molybdic acid is easily recognized when it is not mixed with other coloring oxides, like those of iron, copper and cobalt. Alone on charcoal, with an oxidizing flame, molybdic acid volatilizes almost entirely, becoming brown in contact with red-hot carbon, and on further heating leaving a reddish-brown stain on charcoal. The vapors condense to a coating, yellow when hot, white when cold, crystalline, and which heated an instant by the reducing flame becomes a deep blue; heated to redness, leaves a brownish stain. The natural sulphide gives the same reactions with the odor of sulphur dioxide.

On charcoal, in the reducing flame, molybdic acid becomes brown, then white, and finally is transferred into a gray powder, which is metallic molybdenum, taking a metallic lustre under the agate pestle when separated out by washing and grinding. With carbonate of soda and the oxidizing flame, it fuses rapidly to a nearly colorless glass; in the reducing flame, to a brownish-black glass, and after several minutes reducing, to the gray powder of metallic molybdenum.

With borax in the oxidizing flame, the bead is yellow hot, transparent and uncolored cold. If present in large quantities, the cold bead may be slightly opaque, dark red when hot and bluish when cold. In the reducing flame, the bead is brown and opaque up to the separation out of blackish flakes of molybdenum oxide. In the salt of phosphorous bead, oxidizing flame, the bead is greenish hot, almost colorless cold. In the reducing flame and on charcoal, is dark green hot, but a finer, transparent green cold bead is obtained.

Determination of Molybdenum.

Molybdenum is determined as:

Sulphide, MoS_2, 100 parts of which correspond to 60 of molybdenum or 90 of MoO_3.

Oxide, MoO_2, 100 parts of which correspond to 75 of molybdenum or 112.50 of MoO_3.

Molybdate of cadmium, $CdMoO_4$, 100 parts of which correspond to 35.29 of molybdenum or 52.94 of MoO_3.

Determination as Molybdenum Sulphide.

In analysis, molybdenum is often obtained in solution as a sulphide salt with an excess of sulph-hydrate. Sometimes the question is to examine alkaline molybdates. The latter case may be easily transposed into the first by passing into the neutral or alkaline solution a large excess of hydrosulphuric acid. We will therefore assume that the solution contains sulpho-molybdate, alkaline salts and sulph-hydrate in excess.

The solution is diluted and weak hydrochloric acid added, little by little, until alkaline sulphides are totally decomposed. Heating gently, the hydrosulphuric acid is driven off, and molybdenum sulphide precipitates with a little free sulphur. Waiting until the solution has deposited all the free sulphur in suspension, it is washed by decantation to purify the precipitate from alkaline salts, and dissolved in ammonium sulphide and precipitated afresh in a dilute solution of hydrochloric acid. Molybdenum trisulphide, with a little free sulphur and a little ammonium chloride, results. The precipitate is filtered, dried, the filter paper burned separately, and the precipitate and ash heated in a porcelain crucible placed inside a clay crucible, with carbon in between the two crucibles. The whole is heated gently at first to expel the sulphur and the ammonium chloride, thus avoiding any reaction between them and the molybdenum, the loss as chloride. It should be calcined finally at red heat for ten minutes, the crucible taken out and cooled and weighed. The precipitate thus weighed is MoS_2.

The same exact composition can be arrived at without excess of sulphur by working in a current of hydrogen or pure, dry hydrosulphuric acid. The dried precipitate is placed in a wide, porcelain boat, put into a porcelain combustion tube, the gas current started, heat applied gently at first, while the vapors of ammonium chloride escape. Heat then for ten minutes at low redness in hydrogen or to bright redness in hydrosulphuric acid. The residue is exactly MoS_2.

Determination as Molybdenum Dioxide.

Starting with the alkaline molybdate solution, neutralize the excess of alkali with nitric acid, add mercurous nitrate, obtaining

a yellow precipitate which is almost completely insoluble in the strong excess of mercurous salt. Wash with a nearly-saturated solution of this salt, at first by decantation, then on the filter to remove the alkaline salts. The precipitate formed of molybdate, nitrate, oxide and hydro-carbonate of mercury is removed from the filter, placed in a Rose crucible, and dry hydrogen admitted. After the hydrogen has displaced the air in the crucible, the latter is heated with an alcohol lamp, to decompose the mercurous salts. After heating at low redness for ten minutes, the crucible is cooled and weighed, the molybdenum being found as MoO_2.

This method is much less accurate than the first, which should almost always be preferred. By heating to bright redness in well-dried hydrogen, pure molybdenum may be obtained, as was proven by Von der Pfoerdten; at an intermediate temperature, a compound containing less oxygen than MoO_2 is obtained. The alkaline molybdates may be likewise precipitated by acetate of lead, the precipitate becoming granular or boiling. It is washed first with pure water, then with ammonium nitrate, dried, detached from the filter paper, calcined and weighed.

Determination as Cadmium Molybdate.

Add cadmium nitrate solution to an alkaline molybdate solution almost exactly neutralized by nitric acid. Bring to boiling, filter, wash with pure water, dry, separate the precipitate from the paper, and calcine at a low temperature, treat with a little dilute nitric acid to finish the washing, calcine anew and weigh as cadmium molybdate, $CdMoO_4$.

Determination as Molybdenum Trioxide.

E. Pechard recommends the determination as molybdenum hydrochloride, $MoO_3.2HCl$, or as pure molybdic acid produced by the decomposition of the hydrochloride at 100°. The alkaline molybdate is heated to 440° in a boat in a combustion tube, through which is passed a current of hydrochloric acid gas until the salt is entirely decomposed and transposed into alkaline chloride and a compound of molybdic acid and hydrochloric acid, molybdenum hydrochloride, $MoO_3.2HCl$, which deposits in the neighborhood of the boat in the form of long, white needles,

soluble in water. The solution is evaporated, and at 100° the salt is decomposed, evolving hydrochloric acid and leaving a residue of molybdic acid. It may be weighed in the vessel in which it has been evaporated. There is always a slight bluish coating in the tube formed by the partial reduction of the molybdic acid. It is easily removed by washing with dilute nitric acid, and the method is proceeded with as above.

Tungstic acid forms no volatile compound with hydrochloric acid in this manner, thus permitting the exact separation of molybdenum from tungsten in a mixture of the alkaline salts of their acids. In the analysis of an ammoniacal solution, the heating to 440° entirely eliminates the ammonia.

Precipitation as Sulphide by Hydrogen Sulphide.

In acid solutions this precipitation is slow, and therefore rarely used. It is sometimes advantageous for separating molybdenum from tungsten, such as in lead minerals. By fusion with sodium carbonate, an alkaline solution containing alkali tungstates and molybdates is obtained, which is thus free of metals whose oxides and carbonates are insoluble. Neutralize exactly with hydrochloric acid, add a little tartaric acid to prevent deposition of tungstic acid, pass in hydrosulphuric acid in large excess for twenty-four hours, either in the cold or in a hot-air bath, using a closed flask. The molybdenum sulphide is filtered and the solution treated again with hydrosulphuric acid, to see that there is no further precipitation. The precipitate is redissolved in ammonium sulph-hydrate, then the solution decomposed with hydrochloric acid, and filter out the MoS_2, which is calcined in a current of hydrogen at a very low red heat or in a current of hydrogen sulphide at a bright red heat. To get the tungsten, the first filtrate is evaporated to dryness, adding towards the end of the evaporation nitric acid and sodium nitrate; heat to low redness to destroy tartaric acid, and proceed to the determination of the tungsten in the alkaline solution.

Smith and Bradbury determine molybdenum and tungsten indirectly in the mixture of tungstic and molybdic alkalies. It consists of the precipitation by a cadmium salt and the weighing of the tungstate and molybdate of cadmium together. The precipitate is dissolved in potassium cyanide and electrolyzed,

the cadmium being precipitated. From the weight of the cadmium obtained and the total weight of the cadmium precipitate, the weights of the molybdenum and tungsten can be calculated.

Separation of Molybdenum.

From the alkaline metals.—Precipitate the alkaline molybdate solutions almost entirely neutralized by nitric acid by means of mercurous nitrate in excess. Filter out the mercurous molybdate, wash as has been indicated previously, and treat the precipitate for molybdenum. The alkaline metal is determined in the filtrate by precipitating the mercurous salts by hydrogen sulphide, driving off the excess of hydrogen sulphide by heat, evaporating the alkaline solution, and weighing the residue of alkaline salt.

From the alkaline earth metals.—Fuse the material with three parts of alkali carbonate. Dissolve in water and filter out the alkaline earth carbonates, which remain on the filter and may be determined; the filtrate contains the alkaline molybdate, which may be decomposed by mercurous nitrate as before described. In other cases, the material may be fused with three parts of sodium carbonate and three parts of sulphur, dissolved in water and filtered. The molybdenum will be found in the solution as sulpho-molybdate, which is then decomposed by hydrochloric acid.

From the earth metals (aluminium, chromium, etc.).—Dissolve in hydrochloric acid, dilute and pass in hydrogen sulphide rapidly; saturate with ammonia, add an excess of ammonia sulph-hydrate, and precipitate alumina or oxide of chromium and heat. The molybdenum remains in solution as sulpho-molybdate. Filter and proceed to the separate determination of the alumina and the sulphide of molybdenum.

Molybdenum may, in some cases, be precipitated in acid solutions by hydrogen sulphide if it is done slowly, as we have already stated.

From various metals.—The precipitation of molybdenum in acid solutions by hydrogen sulphide permits of separating it from metals of the first and second groups. For separation from metals of the second group, sulphide of ammonium is used; in the presence of copper, sulphide of sodium is better.

The separation from arsenic is based on the volatility of arsenic sulphide.

Tin sulphide is separated from molybdenum sulphide by boiling with oxalic acid in the presence of hydrochloric acid (Clarke).

The separation of molybdenum from gold and platinum may be made by transposing it into alkaline molybdate, which is soluble in water.

From titanium, tantalum and niobium.—This separation may be made like that of tungsten, by means of ammonium sulphhydrate or per-sulphide of sodium.

From phosphorus and arsenic.—The three acids, molybdic, phosphoric and arsenic being together in alkaline or ammoniacal solutions, the two latter are precipitated by magnesia mixture; the ammoniacal liquor is then saturated with hydrogen sulphide, the sulpho salt formed is decomposed by hydrochloric acid, and molybdenum sulphide precipitated.

The ammonio-magnesium precipitate may retain some molybdenum. It is therefore necessary to repeat the precipitation, or in the presence of arsenic to redissolve the precipitate in hydrochloric acid and to separate the molybdenum by means of a prolonged current of hydrogen sulphide in a hot solution.

Volumetric Determination of Molybdenum.

1. By Permanganate of Potassium.

This method, due to Pisani, is founded on the reduction of molybdic acid in solution in hydrochloric acid by zinc. There is formed a sesqui-oxide salt of molybdenum, coloring the solution dark brown. When this point is reached, the solution is decanted and the residue washed with water. The brown color is then made to disappear by the addition of permanganate, the solution becoming at first green and then colorless; it is entirely oxidized when the rose coloration due to the permanganate appears.

Werncke states that the reduction is never entirely to the state of sesqui-oxide, but to a degree expressed by the formula $Mo_{12}O_{19}$. The experiments of Von der Pfordten have shown that, on the contrary, reduction by zinc may produce an even lower oxide of the formula $Mo_5O_7 = MoO.2Mo_2O_3$; this author

advises the exposing the liquid to the air, which oxidizes the product to the state of sesqui-oxide, and then the operation may be completed as before described.

Material containing about 0.3 grams of molybdenum trioxide is dissolved in a little water containing 50-60 c.c. of 27 per cent. hydrochloric acid; 8-10 grams of zinc, in pieces of which the iron content is accurately known, is introduced. When the liquid has become yellow, it is cooled and poured into a porcelain casserole containing 40 c.c. of dilute sulphuric acid and 20 c.c of a solution of 200 grams of manganese sulphate per liter. Add an equal volume of water and, by means of a burette, enough permanganate solution to produce a feeble rose tint. The result is corrected for the iron in the zinc. The results are quite exact. The permanganate, in place of being titrated by means of ferrous iron or oxalic acid, may be titrated by a known quantity of pure molybdenum or molybdate of ammonia. In this manner, by operating in exactly the same manner in standardizing and titrating, the uncertainty as to the state of oxidation after the reduction by zinc may be removed. The molybdenum content of the ammonium salt may be determined by reduction in a Rose crucible by means of dry hydrogen, first at 170° in an air bath, then at a high temperature over a burner. The ammonia is thus disengaged without loss, and the residue reduced first to MoO_2 and then to pure molybdenum.

2. By Iodide of Potassium.

F. Mauro and L. Danesi propose the estimation of molybdic acid by iodimetry, utilizing the reaction produced on potassium iodide in a concentrated hydrochloric acid solution,

$$MoO_3 + 2HI = MoO_2I + I + H_2O.$$

There is produced a molybdenum oxy-iodide corresponding to the penta-chloride, while a quantity of iodine is liberated proportional to the quantity of molybdenum present. One hundred and twenty-seven parts of free iodine are set free by 144 parts of molybdic anhydride. The reaction takes place in the cold, but it is not complete until the liquid has been heated. The free iodine is titrated with a standard solution of hyposulphite.

The authors advise proceeding as follows: Use 0.2-0.5 gram of molybdate, introduce the material into a glass tube 1 cm. in

diameter and closed at one end, and dissolve it in 2 c.c. of hydrochloric acid of density 1.20. Drive out the air with carbonic acid and put in 1 gram of potassium iodide dissolved in an equal amount of water. Seal the tube and heat in boiling water for ninety minutes. When cold, open the tube, add water and wash into a casserole with cold water. Estimate the iodine with a 1-20N solution of hyposulphite, run in from a burette, until the red-brown color becomes faint. Then add a little starch paste and complete the titration. When the last traces of the free iodine have disappeared, the dark tint of the solution gives place to a very clear orange. The operation is rapid and the results are concordant.

Analysis of Molybdenite.

Take one gram of finely-pulverized material and digest with a concentrated solution of caustic potash. Heat to 100° and pass in a current of chlorine, which aids in the solution of the sulphide. Filter, to remove gangue, and wash the residue. Add to the solution a little hydrochloric acid and heat to drive off the chlorine. Precipitate the sulphuric acid by chloride of barium, wash the precipitate with cold water, dry, calcine and weigh, and from it calculate the sulphur content of the ore.

To determine the molybdenum, treat one gram of the ground mineral with aqua regia diluted with water. Add ammonia and ammonium sulph-hydrate. Filter, to separate the gangue and residue of insoluble sulphides, which may be analyzed apart. The filtered liquor is acidified with hydrochloric acid precipitating molybdenum sulphide, filtered, dried at 100°, mixed with a little sulphur, and calcined slowly at redness. Allow to cool, and weigh.

Molybdenum may also be determined in molybdenite by the following method: Take one gram of ore, add three grams of caustic soda and one gram of sodium peroxide, fuse in a silver crucible, heat slowly to low redness. Take up with boiling water and wash into a porcelain dish, neutralize with hydrochloric acid, and then make slightly alkaline with ammonia. Add cadmium nitrate solution, bring to boiling, filter, wash, dry, calcine, and weigh as cadmium molybdate.

Analysis of Wulfenite.

Take five grams of well-ground ore, digest in concentrated nitric acid, heat slightly, and when the attack is complete, add ammonia in excess and ammonium sulphide. Let stand, and then filter out the silica and the insoluble sulphides and in the filtrate precipitate molybdenum sulphide by the addition of nitric acid.

The process of Pechard may also be used, treating the powdered ore in a current of chlorine in a tube heated to redness. The molybdenum hydrochloride is caught in water and molybdic acid precipitated from it as has already been explained. Since lead chloride carried over by volatilization is not entirely insoluble in water, a few drops of sulphuric acid are used in the solution to precipitate the lead as sulphate.

Analysis of Molybdenum and Ferro-Molybdenum.

Two grams of metal in the shape of turnings or drillings are dissolved in nitric acid; the residue is filtered and to it an excess of mercurous nitrate is added. The molybdenum is precipitated as a sulphur-yellow, mercurous molybdate. Wash with a saturated solution of mercurous nitrate and filter. Dry, remove the precipitate from the paper, calcine in a Rose crucible at a low red heat in a current of hydrogen, let cool and weigh. The carbon is determined in 5-10 grams by volatilizing the iron and molybdenum in a current of chlorine at low redness, and followed by burning the residue in a current of oxygen, catching the carbon dioxide. Iron is determined by ordinary methods. If it is desired to determine the amount of iron in combination with molybdenum, the metal may be treated in a porcelain dish with 10 times its weight of double chloride of copper and potassium, which dissolves the iron but not the ferro-molybdenum. Dilute to 100-200 c.c. with hot water, add 10 c.c. hydrochloric acid, heat to 80° until the iron is dissolved, and filter through asbestos in a Gooch crucible.

Determination of Molybdenum in Steel.

Method of Carnot.—Dissolve 10 grams of metal, in the form of borings or turnings, in hydrochloric acid, decant from the

insoluble residue, put a few drops of hydrochloric and nitric acids on the residue, and evaporate to dryness. Wash with water, filter, dry and weigh the insoluble silica. Unite the filtrates and reduce by sulphur dioxide, driving off the excess by boiling. Pass a current of hydrogen sulphide until precipitation is complete. Filter, dry the precipitate, mix with a little sulphur, and heat in a current of hydrogen, so as to volatilize arsenic sulphide. The molybdenum sulphide remains as MoS_2, with 60 per cent. molybdenum.

Variation of Chalard.—After dissolving 5 grams of metal in hydrochloric acid and oxidizing by nitric acid, neutralize exactly with sodium carbonate, filter, and put the filter and precipitate in a flask containing 100-150 c.c. of 2N solution of caustic soda. Heat to boiling until the molybdenum is completely dissolved, dilute to 500 c.c. and take out 250 c.c. Neutralize this with hydrochloric acid, add lead acetate and ammonium acetate in excess. Warm, filter in a Gooch crucible, wash the precipitate, calcine, and weigh as lead molybdate, $PbMoO_4$.

Analysis of Molybdenum Silicides.

1. By Chlorination.

Weigh out one gram of pulverized material, put in a tube of Bohemian glass connected with a cooled condenser, heat to redness and pass chlorine through. Tetrachloride of silicon forms along with pentachloride of molybdenum. Cool the solution in the condenser, add nitric acid, evaporate to dryness, and there results a mixture of silica and molybdic acid. Place this mixture again in the tube and pass chlorine through, resulting in the converting of the molybdic acid into oxychloride, which sublimes and is caught in water. The residue is pure silica, which is weighed. The solution of molybdenum oxychloride is brought to boiling and evaporated to dryness. This reforms molybdic acid, which may be dissolved in ammonia to separate it from oxide of iron. Precipitate the molybdenum in solution as lead molybdate, filter, dry and weigh.

The mixture of silica and molybdic acid may also be heated to 360° in a current of hydrochloric acid gas, producing the volatile molybdenum hydrochloride, which is caught in water.

This solution is evaporated to dryness, which regenerates molybdic acid.

2. By Sodium Peroxide.

One gram of the silicide is pulverized and intimately mixed with 10 grams of sodium carbonate and 3 grams of sodium peroxide, placed in a silver capsule and slowly heated. When the attack is completed, take up with boiling water and precipitate with dilute hydrochloric acid. Evaporate to dryness, wash with acidulated water, dry and calcine. Place the mixture of silicic acid and molybdic acid in a tube and treat with hydrochloric acid gas as above described.

Method of Ibotson and Brearly.

For Molybdenum in Metallurgical Products.—To determine small amounts of molybdenum in steel or in ferro-molybdenum, dissolve about 2 grams in hydrochloric acid, oxidize with nitric acid or potassium chlorate, add sodium carbonate to neutralize the larger part of the acid, until a coloration appears or a red precipitate begins to form. Place in a casserole containing 40-50 c.c. of 2N sodium hydroxide, more than is necessary to precipitate all the iron. It is easy to calculate the quantity of soda which should be used, knowing that 1 gram of iron as ferric chloride requires 54 c.c. of normal soda for its complete precipitation. The liquid holding the precipitate in suspension is heated to boiling, filtered, and the filtrate is acidified with hydrochloric acid. The molybdenum is then precipitated as molybdate of lead, as we have previously indicated.[5] Redissolve the molybdate of lead in hydrochloric acid, to take out any small quantities of silica which it contains, and reprecipitate. This method gives good results on cast-iron containing 3-4 per cent. of molybdenum, but it is preferable in this case to eliminate graphite by filtration. Incinerate the precipitate at low redness and fuse the residue with potassium nitrate.

The estimation of molybdenum in steel by the above method is not interfered with by the presence of elements ordinarily found in steel excepting tungsten.

It is interesting to give the influence which molybdenum exerts on the estimation of the other elements present in steel.

[5] Chem. News, **78**, 203.

Silicon.—Molybdenum is without influence.

Manganese.—Molybdenum does not interfere when manganese is precipitated by bromine and ammonia, if the iron is separated by ammonium acetate and a large excess of acetate used, as almost all of the molybdenum is precipitated with the iron. But the results are too low when the molybdenum is determined by the volumetric method, oxidizing by potassium chlorate in a nitric acid solution. A specimen of steel with 0.6 per cent. of manganese gave, in this way, only 0.39 per cent., but by adding double as much chlorate as before, all the manganese was obtained.

Sulphur.—The gravimetric determination of sulphur gives good results if barium chloride is added to an acid solution, which prevents the formation of barium molybdate or iron molybdate. Molybdenum is without influence on the estimation of sulphur evolved as hydrogen sulphide and absorbed by metallic solutions if strong hydrochloric acid is used for driving it off.

Phosphorus.—The molybdate (acetate) method gives good results. The rapid method of precipitation of phosphorus in the presence of iron gives too high figures, partly because molybdic acid goes in the yellow precipitate. This difficulty may be surmounted by dissolving the phospho-molybdate in ammonia and reprecipitating the phosphorus by magnesia mixture.

Carbon.—The carbonaceous residue formed by decomposing by copper solutions gives blue wash-waters containing Mo_3O_8, even after the copper salts have been completely washed out. The results compared with those by combustion with lead peroxide are several hundredths of a per cent. too low.

Iron.—In precipitating with aqua ammonia, a part of the molybdenum comes down with the iron. The iron cannot be determined by solution and titration, because the molybdenum is reduced by nascent hydrogen to the stage of Mo_2O_3 and causes wrong results, as it is peroxidized back again to the state of MoO_3. Ferric solutions should not be reduced by zinc or stannous chloride, but may be reduced by sulphurous acid, which does not reduce molybdenum, and then proceeding to the volumetric determination by bichromate or permanganate. Ferro-

cyanide of potassium does not give a close indication with ferric salts in the presence of molybdenum because of the formation of a dark-brown precipitate with molybdic solutions.

Analysis of Ferro-molybdenum and of "Cast" Molybdenum.

These alloys are easily attacked by acids and may be analyzed by the above described methods.

Analysis of Nickel-molybdenum.

This alloy contains usually a small quantity of iron. It is dissolved in aqua regia and the solution run into an excess of ammonia. When the alloy contains more than a few tenths of a per cent. of iron, the precipitate obtained will carry small quantities of nickel and molybdenum, from which it is freed by filtration, resolution and reprecipitation. The molybdenum is precipitated in a fractional part of the filtrate without it being necessary to separate out the nickel. The nickel may be determined volumetrically by cyanide, even in the presence of molybdenum. When the iron is in large quantities, molybdenum should be separated, as in molybdenum steels, by means of sodium hydrate. In a separate portion, iron and nickel are precipitated to determine the latter, which can be done easily by means of ammonia, for basic ferric molybdate precipitates only long before the solution becomes alkaline.

Analysis of Molybdenum Powder.

This powder contains, along with molybdenum, molybdic acid, mixtures of the lower oxides of molybdenum, tungsten, tungstic oxides, silica, alumina, ferric oxide, combined carbon, graphite, sulphur and water.

Oxygen.—The best commercial powders are gray and anhydrous, the lower grade powders are black and contain 5-6 per cent. of water. All of them contain more or less MoO_2, MoO_3 and Mo_3O_8. It is not known how to separate these different oxides.

The blue oxide, Mo_3O_8, and its hydrate are soluble in water. The powder can be washed with water, and the Mo_3O_8 present in the black, hydrated varieties thus determined. By boiling

one gram of the powder ten minutes in 100 c.c. of 2N caustic potash, filtering and precipitating the molybdenum in the filtrate, the MoO_3 can be determined, since metallic molybdenum and combinations of Mo_2O_3 and MoO_2 are insoluble in caustic potash. Sometimes the filtered liquid from the treatment of the powder gives a precipitate of lead sulphide when lead acetate is added to precipitate the molybdenum. In this case, it is necessary to acidify the liquid and drive off the hydrogen sulphide before the precipitation by lead.

Molybdenum and molybdenum dioxide reduce ammoniacal silver solutions, six atoms of silver being precipitated by one of molybdenum; on this may be based an approximate method of determining the greater or less purity of a specimen of molybdenum.

Carbon.—Carbon may be easily determined by direct combustion in a current of oxygen. Moissan determined combined carbon by attacking the substance by acids, passing the gas evolved over hot copper oxide and catching it in caustic potash; graphite was determined in the insoluble residue.

Molybdenum.—The metal is mixed with carbonate of soda and a small quantity of potassium nitrate and covered with a layer of carbonate, heated to complete decomposition, the bottom only of the crucible being heated to redness, so as to avoid volatilization of molybdic acid. Take up with water, precipitate in the filtered liquid molybdenum and tungsten by lead acetate. Separate the two elements by the method already mentioned.[6]

Molybdenum may also be determined by dissolving 3-5 grams in aqua regia, evaporating to dryness and boiling the residue strongly with concentrated hydrochloric acid. Dilute and filter; the residue may contain some tungstic acid and some molybdic acid with the silica. It is calcined at a low temperature, fused with potassium nitrate, taken up with water, and added to the principal solution. In part of the latter, iron and alumina are precipitated by ammonia, and the molybdenum and tungsten determined. In another portion, sulphur and other elements may be determined.

[6] Chem. News, 81, 13.

Method of Muller and Van Dyke Cruser for Determination of Molybdenum in Steels and Alloys.

Dissolve the steel in nitric acid, add sulphuric acid. heat to sulphuric fumes, and precipitate sulphide of molybdenum by hydrogen sulphide. Filter, redissolve the molybdenum sulphide by hydrochloric acid, then add nitric and sulphuric acids. Add ammonia in excess, filter and titrate the filtrate by potassium permanganate. Ferro-molybdenum may be similarly treated. When the alloy contains tungsten, add tartaric acid to the acid solution, boil, and the tungsten, vanadium and uranium go into solution. These authors think that the analyses made by ammonia or by solutions in it give too high results and that the determination as lead molybdate as given requires too much time.

The Composition of Several Alloys of Molybdenum.

	Powdered Molybdenum		Nickel Molybdenum		Ferro Molybdenum	Cast Molybdenum
Molybdenum	72.62	86.72	70.53	36.25	16.69	92.40
Tungsten	3.17	. .	1.27	. .	1.53	0.74
Nickel	. .	. .	21.60	57.80	. .	. .
Iron	1.60	0.48	3.08	1.60	76.34	2.73
Carbon	7.80	8.18	2.94	1.08	4.20	3.87
Silicon	. .	. .	0.42	0.14	0.39	0.05
Manganese	. .	. .	0.40	trace	0.37	. .
Silica	. .	1.57	. .	. .	. .	. .
Sulphur	. .	0.10	trace	3.00	0.076	0.33
Oxygen	8.30	1.00	. .	. .	. .	. .
Water	4.30	. .	. .	. .	. .	. .

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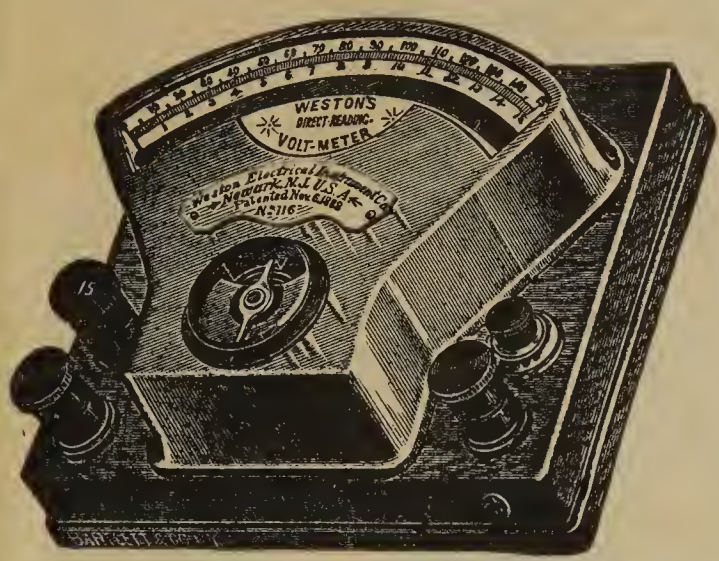

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